

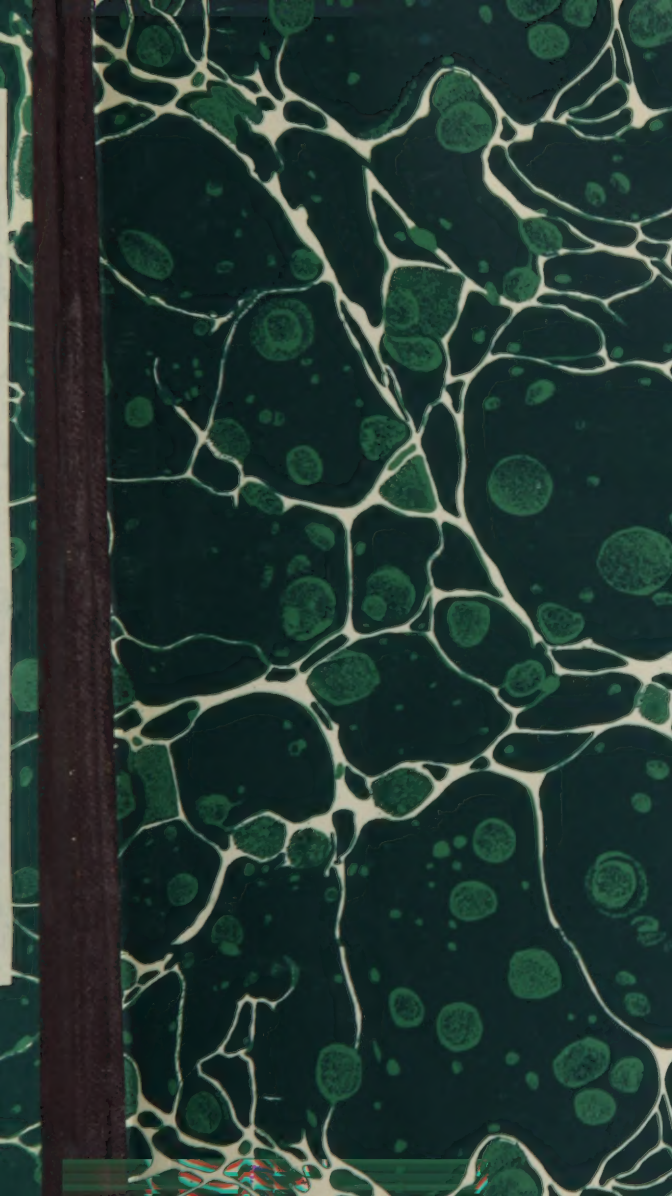
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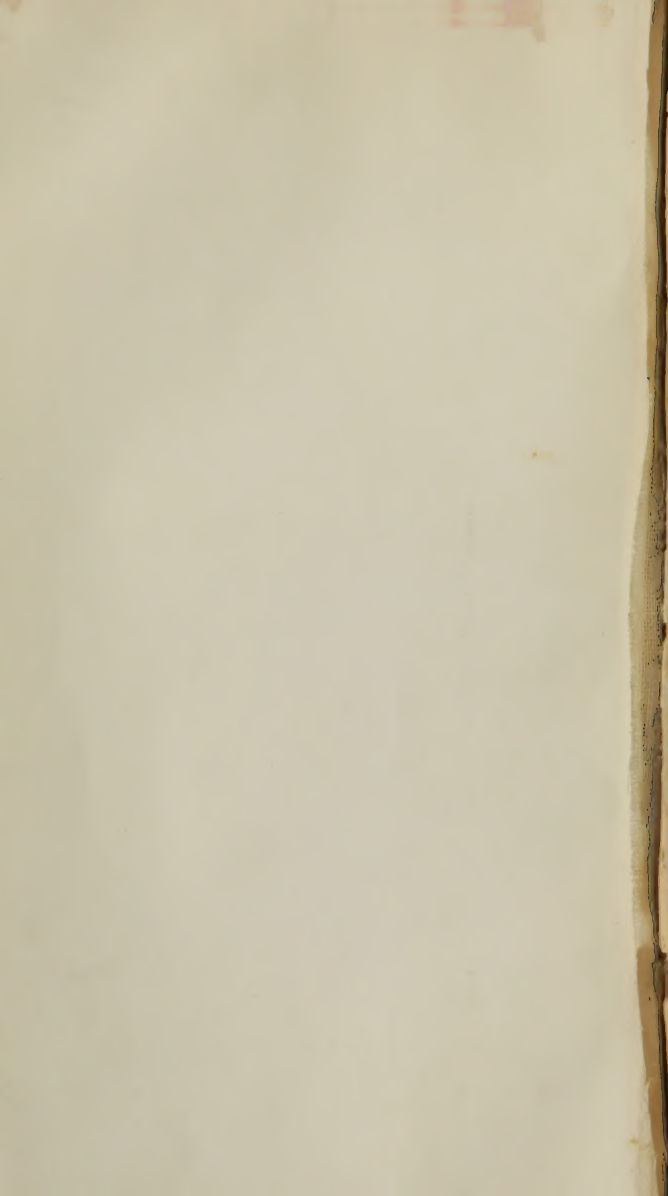


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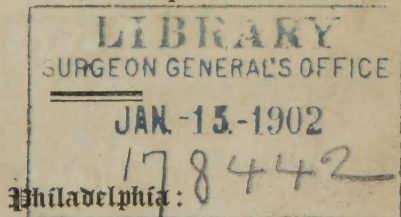
RECENT DISCOVERIES AND DOCTRINES OF THE SCIENCE.

BY

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*Second American Edition, with Important Corrections.*



JOHN GRIGG, NO. 9, NORTH FOURTH STREET,

*Printed by James Kay, Jun. & Co.*

1829.

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*Clerk of the Eastern District of Pennsylvania.*

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TO

FREDERICK STROMEYER, M.D. F.R.S.E.

PROFESSOR OF CHEMISTRY IN THE UNIVERSITY

OF GÖTTINGEN, &c. &c. &c.

MY DEAR SIR,

UNDER your guidance I made my first essay in Analytical Chemistry ; from your example I imbibed a taste for Chemical research ; and to you I am indebted for that practical knowledge of the subject, without which this Volume would never have been written. To you, therefore, who have thus so essentially contributed to the undertaking, permit me to inscribe a Work intended to advance the progress of that science which you cultivate with so much zeal and success. Believe me, my dear Sir, this opportunity of publicly expressing my gratitude for your kindness, and my admiration of your distinguished analytical attainments, is a source of much pride and pleasure to your Friend, and former Pupil,

EDWARD TURNER.

EDINBURGH,  
*February, 1, 1827.*



## PREFACE.

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**T**HE following pages comprehend a condensed view of the present state of Chemical Science. The chief purpose of the work is to make the Student intimately acquainted with the theory, at the same time that he is acquiring a knowledge of the facts of Chemistry ; so that, by the establishment of fixed principles, the details may more easily be impressed on the memory, and excite an interest which they would not otherwise possess. Every one, who is acquainted with modern Chemistry, will admit that the study of the Laws of Combination is fitted in a peculiar manner for promoting these objects ; and hence, I have treated at length of the Atomic Theory, and the subjects connected with it, at an early part of the Volume.

To this arrangement, I am aware, it may be objected, that many of the facts adduced as illustrations must necessarily be unknown to the beginner. I do not anticipate, however, any serious inconvenience from this source ; on the contrary, some experience in teaching the theoretical and practical details of the Science, gives me reason to think that the disadvantages of my plan will be very far outweighed by its advantages. I may observe, indeed, that this work is chiefly designed for persons who have either attended, or are attending Lectures on Chemistry ; and, to such readers, the objection to which I allude, does not apply.

In the composition of this work, I have had recourse, as far as possible, to the original sources of information ; but



I have also derived much assistance from the elements of Sir H. Davy, and Dr Henry ; from the Systems of M. Thénard, and the late Dr Murray ; and from the System and First Principles of Dr Thomson. I should also add, that the materials of the Small Treatise, published about eighteen months ago, on the Laws of Combination and the Atomic Theory, are, with slight modifications, incorporated in the present Volume.

This Treatise, however, is not to be viewed in the light of a mere compilation. In the purely practical parts of the Work, for example, in describing processes, in giving the tests for demonstrating the presence of substances, and in explaining the rules for conducting Chemical Analysis, I have in general merely stated in writing what I am in the habit of practising in the Laboratory. It is likewise proper to mention, that, in detailing the experimental results obtained by other Chemists, I have in many instances verified them by my own observation ; and when treating of the obscure or disputed parts of the Science, I have taken pains to render the former clear, and to distinguish in the latter what is ascertained, from what is still undetermined.

EDINBURGH, *Feb.* 1, 1827.



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## INTRODUCTION.

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**M**ATERIAL substances are endowed with two kinds of properties, physical and chemical; and the study of the phenomena occasioned by them has given rise to two corresponding branches of knowledge, Natural Philosophy and Chemistry.

The physical properties are either general or secondary. The first are so called because they are common to all bodies; the latter from being observable in some substances only. Among the first are commonly ranked extension, impenetrability, mobility, extreme divisibility, gravitation, and porosity.

Extension is the property of occupying a certain portion of space. A substance is said to be extended when it possesses length, breadth, and thickness. By impenetrability is meant that no two portions of matter can occupy the same space at the same moment. Every thing that possesses extension and impenetrability is matter.

Matter, though susceptible of motion, has no power either to move itself, or arrest its progress when an impulse is once communicated to it. This indifference to rest or motion has been expressed by the term *vis inertiae*, as if it depended on some specific force resident in matter; but it may with greater propriety be regarded as a negative character, in consequence of which matter is wholly given up to the operation of the various forces which are constantly acting upon it.

Matter is divisible to an extreme degree of minuteness. A grain of gold may be beaten out into so fine a leaf as to cover 50 square inches of surface, and contain two millions of visible points; and yet the gold which covers the silver wire, used in making gold lace, is spread over a surface twelve times as great. (Nicholson's Introduction to Natural Philosophy, vol. i.)

All bodies descend in straight lines towards the centre of the earth when left at liberty at a distance from its surface. The power which produces this effect is termed gravity, the attraction of gravitation, or terrestrial attraction; and the force required to separate a body from the surface of the earth, or prevent it from descending towards it, is called its weight. Every particle of matter is equally affected by gravity; and therefore the weight of any body will be proportional to the number of ponderable particles which it contains.

The minute particles of which bodies consist are disposed in such a manner as to leave certain intervals or spaces between them, an arrangement which is called porosity. These interstices can sometimes be seen by the naked eye, and frequently by the aid of glasses. But

were they wholly invisible, it would still be certain that they exist. All substances, even the most compact, may be diminished in bulk either by mechanical force or a reduction of temperature. It hence follows that their particles must touch each other at a very few points only, if at all; for if their contact was so perfect as to leave no interstitial spaces, then it would be impossible to diminish the dimensions of a body, because matter is incompressible and cannot yield.

The secondary properties of matter are opacity, transparency, softness, hardness, elasticity, colour, density, solidity, fluidity, and the like. The condition of bodies with respect to several of these properties seems dependent on the operation of two opposite forces—cohesion and repulsion. To understand how the particles of a body can attach themselves to one another and form a whole, we must suppose them endowed with a power of reciprocal attraction. This force is called cohesion, cohesive attraction, or the attraction of aggregation, in order to distinguish it from terrestrial attraction. Gravity is exerted between different masses of matter, and acts at sensible and frequently at very great distances; while cohesion exerts its influence only at insensible and infinitely small distances. It enables similar molecules to cohere, and tends to keep them in that condition. It is best exemplified by the resistance which a hard body, as iron or marble, affords to being broken by any external force.

The tendency of cohesion is manifestly to bring the ultimate particles of bodies into immediate contact; and such would be the result, were it not counteracted by an opposing force, a principle of repulsion, which prevents their approximation. It is a general opinion among philosophers, supported by very strong facts, that this repulsion is owing to the agency of caloric, which is somehow attached to the elementary molecules of matter, causing them to repel one another. Material substances are therefore subject to the action of two contrary and antagonizing forces, one tending to separate their particles, the other to bring them into closer proximity. The form of bodies, as to solidity and fluidity, is determined by the relative intensity of these powers. Cohesion predominates in solids, in consequence of which their particles are prevented from moving freely on one another. The particles of a fluid, on the contrary, are far less influenced by cohesion, being free to move on each other without friction. Fluids are of two kinds, elastic fluids or aeriform substances, and inelastic fluids or liquids. Cohesion seems wholly wanting in the former; they yield readily to compression, and expand when the pressure is removed; indeed, the space they occupy is solely determined by the force which compresses them. The latter, on the contrary, do not yield perceptibly to ordinary degrees of compression, nor does an appreciable dilatation ensue from the removal of pressure, the tendency of repulsion being counterbalanced in them by cohesion.

Matter is subject to another kind of attraction different from those yet mentioned, termed chemical attraction or affinity. Like cohesion it acts only at insensible distances, and thus differs entirely from gravity. It is distinguished from cohesion by being exerted between dissimilar particles only, while the attraction of cohesion unites similar particles. Thus, a piece of marble is an aggregate of smaller portions of marble attached to one another by cohesion, and the parts so attached are called integrant particles; each of which, however minute, is as perfect marble as the mass itself. But the integrant particles consist of two substances, lime and carbonic acid, which are

different from one another as well as from marble, and are united by chemical attraction. They are the component or constituent parts of marble. The integrant particles of a body are therefore aggregated together by cohesion; the component parts are united by affinity.

The chemical properties of bodies are owing to affinity, and every chemical phenomenon is produced by the operation of this principle. Though it extends its influence over all substances, yet it affects them in very different degrees, and is subject to peculiar modifications. Of three bodies, A, B, and C, it is often found that B and C evince no affinity for one another, and therefore do not combine; that A, on the contrary, has an affinity for B and C, and can enter into separate combination with each of them; but that A has a greater attraction for C than for B, so that if we bring C in contact with a compound of A and B, A will quit B and unite by preference with C. The union of two substances is called combination; and its result is the formation of a new body endowed with properties peculiar to itself, and different from those of its constituents. The change is frequently attended by the destruction of a previously existing compound, and in that case decomposition is said to be effected.

The operation of chemical attraction, as thus explained, obviously lays open a wide and interesting field of inquiry. One may study, for example, the affinity existing between different substances; an attempt may be made to discover the proportion in which they unite; and finally, after collecting and arranging an extensive series of insulated facts, general conclusions may be deduced from them. Hence chemistry may be defined the science, the object of which is to examine the relations that affinity establishes between bodies, ascertain with precision the nature and constitution of the compounds it produces, and determine the laws by which its action is regulated.

Material substances are divided by the chemist into simple and compound. He regards those bodies as compound which can be resolved into two or more parts, and those as simple or elementary, which contain but one kind of ponderable matter. The number of the latter amounts only to fifty-one; and of these all the bodies in the earth, as far as our knowledge extends, are composed. The list, a few years ago, was somewhat different from what it is at present; for the acquisition of improved methods of analysis has enabled chemists to demonstrate that some substances, which were once supposed to be simple, are in reality compound; and it is probable that the same will hereafter be proved of some of those, which are at present regarded as simple.

The composition of a body may be determined in two ways, analytically or synthetically. By the first method, the elements of a compound are separated from one another, as when water is resolved by the agency of galvanism into oxygen and hydrogen; by the second, they are made to combine, as when oxygen and hydrogen unite by the electric spark, and generate a portion of water. Each of these kinds of proof is satisfactory; but when they are conjoined,—when we first resolve a particle of water into its elements, and then reproduce it by causing them to unite, the evidence is quite irresistible.

I have followed, in the composition of this Treatise, the same general arrangement which I adopt in my lectures. It is divided into four principal parts. In the first, I shall treat of the Imponderables,—agents of so diffusible and subtile a nature, that the common attributes of matter cannot be perceived in them. They are altogether destitute of weight; at least, if they possess any, it cannot be discovered by our

most delicate balances. They cannot be confined and exhibited in mass like ordinary bodies; they can be collected only through the intervention of other substances. Their title to be considered material is therefore questionable, and the effects produced by them have accordingly been attributed by some to certain motions or affections of common matter. It must be admitted, however, that they appear to be subject to the same powers that act on matter in general, and that some of the laws which have been determined concerning them, are exactly such as might have been anticipated on the supposition of their materiality. It hence follows, that we need only regard them as subtile species of matter, in order that the phenomena to which they give rise may be explained in the language, and according to the principles which are applied to material substances in general; and I shall therefore consider them such in my subsequent remarks.

The second part comprises Inorganic Chemistry. It includes the doctrine of affinity, and the laws of combination, together with the chemical history of all the elementary principles hitherto discovered, and of those compound bodies which are not the product of organization. The elementary bodies are divided into the non-metallic and metallic; and the substances contained in each division are treated in the order which, it is conceived, will be most convenient for the purposes of teaching. From the important part which oxygen plays in the economy of nature, it is necessary to begin with the description of that principle; and from the tendency it has to unite with other bodies, as well as the importance of the compounds it forms with them, it will be useful, in studying the history of each elementary body, to describe the combinations into which it enters with oxygen gas. The remaining compounds which the non-metallic substances form with one another, will next be considered. The description of the individual metals will be accompanied by a history of their combinations, first with the simple non-metallic bodies, and afterwards with one another. The student will thus be prepared for the study of the salts. This arrangement is recommended by its simplicity and convenience, and by not being founded on any particular theory. I have deviated from the usual practice of dividing elementary substances into supporters of combustion and combustibles, or into electro-negative and electro-positive bodies; and my reasons for doing so are, that I have been unable either to convince myself that an arrangement founded on these principles is free from objection in theory, or to perceive its advantage in facilitating the study of the science.

The third general division of the work is on Organic Chemistry, a subject which will be conveniently discussed under two heads, the one comprehending the products of vegetable, the other of animal life.

The fourth part contains brief directions for the performance of analysis.

# ELEMENTS

OF

# CHEMICAL SCIENCE.

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## PART I.

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### SECTION I.

#### *CALORIC.*

**T**HE term Heat, in common language, has two meanings; in the one case, it implies the sensation we experience on touching a hot body; in the other, it expresses the cause of that sensation. As this vagueness of expression is ill suited to the purposes of science, it has been proposed to employ the word Caloric to signify the principle of heat, and the employment of it has now become general.

Caloric, on the supposition of its being material, is a subtile fluid, the particles of which repel one another, and are attracted by all other substances. It is imponderable; that is, it is so exceedingly light that a body undergoes no appreciable change of weight, either by the addition or abstraction of caloric. It is present in all bodies, and cannot be wholly separated from them. For if we take any substance whatever, at any temperature, however low, and transfer it into an atmosphere, whose temperature is still lower, a thermometer will indicate that caloric is escaping from it. That its particles repel one another, is proved by observing that it flies off from a heated body; and that it is attracted by other substances, is equally manifest from the tendency it has to penetrate their particles, and be retained by them.

Caloric may be transferred from one body to another. Thus, if a cup of mercury at  $60^{\circ}$  be plunged into hot water, caloric passes rapidly from one into the other, until the temperature in both is the same; that is, till a thermometer placed in each of them stands at the same height. All bodies on the earth are constantly tending to attain an equality, or what is technically called an equilibrium of temperature. If, for example, a number of substances, different in temperature, be enclosed in an apartment, in which there is no actual source of caloric, they will very soon acquire an equilibrium, so that a thermometer will stand at the same point in all of them. The varying sensations of heat



and cold, which we experience, are owing to a like cause. On touching a hot body, caloric passes from it into the hand, and excites the feeling of warmth; when we touch a cold body, caloric is communicated to it from the hand, and thus produces the sensation of cold.

As the transportation of caloric is constantly going forward, it is important to determine by what means, and according to what laws, the equilibrium is established. When any substance is brought into contact with another, which differs from it in temperature,—if, for example, a cold bar of iron be thrust among glowing embers, or a hot ball of the same metal be plunged into a basin of cold water,—the excess of caloric in the hot body passes rapidly to the particles on the surface of the other; from them it is transferred to those situated more internally, and so forth, till the bar in the one case, and the ball in the other arrive at the same temperature as the embers or the water with which they are in contact. In such instances, caloric is said to pass by communication, or to be communicated from one body to another; and in its passage through any one of those bodies, it is said to be conducted by them.

But when a heated substance is placed under such circumstances as to preclude the possibility of its caloric being communicated,—for instance, when a glass globe full of hot water is suspended in the vacuum of an air-pump,—the excess of its caloric still passes away, and in a very short time it will have acquired the temperature of the surrounding objects. It must then be capable of passing from one body to another situated at a sensible distance; it is projected as it were from one to the other. In order that its passage should take place in this manner, it is not necessary that the body should be in vacuo; it passes with equal facility through the air as through a vacuum.

It follows, therefore, that in establishing an equilibrium of temperature, caloric is distributed among the surrounding objects in two ways; partly through the means of intermediate bodies, or by communication, partly in consequence of an interchange established from a distance, or by radiation.

### *Communication of Caloric.*

Caloric passes through bodies with different degrees of velocity. Some substances oppose very little impediment to its passage, while it is transmitted slowly by others. Daily experience teaches, that though we cannot leave one end of a rod of iron for some time in the fire, and then touch its free extremity, without danger of being burnt; yet this may be done with perfect safety with a rod of glass or of wood. The caloric will speedily traverse the iron bar, so that at the distance of a foot from the fire, it is impossible to support its heat; while we may hold a piece of red hot glass two or three inches from its extremity, or keep a piece of burning charcoal in the hand, though the part in combustion is only a few lines removed from the skin. The observation of these and similar facts has led to a division of bodies into conductors and non-conductors of caloric. The former division, of course, includes those bodies which allow caloric to pass freely through their substance, such as metals; and the latter comprises those which do not give an easy passage to it, such as stones, glass, wood and charcoal.

Various methods have been adopted for determining the relative conducting power of different substances. The most convenient is



that of Ingenhouz\*. He covered little rods of the same form, size, and length, but of different materials, with a layer of wax, plunged their extremities into heated oil, and noted to what distance the wax was melted on each during the same interval. The metals were found, by this method, to conduct caloric better than any other substances; and of the metals, silver is the best conductor; gold comes next, then tin and copper, which are nearly equal; then iron, platinum and lead.

An ingenious plan was adopted by Count Rumford† for ascertaining the relative conducting powers of the different materials employed for clothing. He enveloped a thermometer in a glass cylinder blown into a ball at its extremity, and filled the interstices with the substance to be examined. Having heated the apparatus to the same temperature in every instance by immersing it in boiling water, he transferred it into melting ice, and observed carefully the number of seconds which elapsed during the passage of the thermometer through 135 degrees. When there was air between the thermometer and cylinder, the cooling took place in 576 seconds; when the interstice was filled with fine lint, it took place in 1032"; with cotton wool in 1046"; with sheep's wool in 1118"; with raw silk in 1284"; with beaver's fur in 1296"; with eider down in 1305'; and with hare's fur in 1315'. The general practice of mankind is therefore fully justified by experiment. In winter we retain the animal heat as much as possible by covering the body with bad conductors, as silk or woollen stuffs; in summer we have recourse to cotton or linen articles with an opposite intention.

A variety of familiar phenomena arise from the difference of conducting powers; thus, if a piece of iron and of glass be heated to the same degree, the sensation they communicate to the hand is very different; the iron will give the sensation of burning, while the glass feels but moderately warm. The quantity of caloric, which in a given time may be brought to the surface of the heated body, so as to pass into the skin, is much greater in the iron than in the glass, and therefore in the former case the sensations must be more acute. This proves that our sense of touch is a very fallacious test of heat and cold; and hence, when we apply the hand to various objects in our apartment, we are very apt to form wrong notions of their temperature. The carpet will feel nearly as warm as our body; our book will feel cool, the table cold, the marble chimney-piece colder, and the candlestick colder still; yet, a thermometer applied to them will stand in all at exactly the same elevation. They are all colder than the hand; but those that carry away caloric most rapidly, excite the strongest sensations of cold.

The conducting power of solid bodies does not seem to be related to any of the other properties of matter; but it approaches nearer to the ratio of their densities than to that of any other property. Count Rumford found a considerable difference in the conducting power even of the same material, according to the state in which it was employed. His observations seem to warrant the conclusion, that in the same substance the conducting power increases with the compactness of structure.

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\* Ingenhouz, *Journal de Phys.* 1789, p. 63.

† Rumford, *Phil. Tr.* 1792.

Liquids may be said, in one sense of the word, to have the power of communicating caloric with great rapidity, and yet they are very imperfect conductors. The transmission of caloric from particle to particle does in reality take place very slowly; but in consequence of the mobility of their particles upon each other, there are peculiar internal movements, which, under certain circumstances, may be occasioned in them by the application of heat, and which do more than compensate for the imperfect conducting power with which they are really endowed.

When certain particles of a liquid are expanded by heat, they become specifically lighter than those which have not yet received an increase of temperature; and consequently, according to a well-known law in physics, they must rise towards the upper surface of the liquid, while their place is supplied by the adjoining particles, which are colder and denser, and therefore disposed to descend. It follows that if heat be applied to the bottom of a vessel containing any liquid, a double set of currents must be immediately established, the one of hot particles rising towards the surface, and the other of colder particles descending to the bottom. Now, these currents take place with such rapidity, that if a thermometer be placed at the bottom, and another at the top of a long jar, the heat being applied below, the upper one will begin to rise almost as soon as the lower. Hence, under certain circumstances, caloric is rapidly communicated through fluids.

But if, instead of applying heat to the bottom of the jar, the caloric is made to enter by the upper surface, very different phenomena will be observed. The intestine movements cannot now be formed, because the heated particles have a tendency to remain constantly at the top; the heat can descend through the fluid only by transmission from particle to particle, a process which takes place so very tardily, as to have induced Count Rumford to deny that water could conduct at all. In this he was mistaken; for the opposite opinion has been successfully supported by Dr Hope, Dr Thomson, and the late Dr Murray, though they all admit that water, and liquids in general, mercury excepted, possess the power of conducting caloric in a very slight degree.

It is very difficult to estimate the conducting power of aeriform fluids. Their particles move so freely on each other, that the moment a particle is dilated by heat, it is pressed upwards with great velocity by the descent of colder and heavier particles, so that an ascending and descending current is instantly established. Besides, these bodies allow a passage through them by radiation. Now, the quantity of caloric which passes by these two channels is so much greater than that which is conducted from particle to particle, that we possess no means of determining their proportion. It is certain, however, that the conducting power of gaseous fluids is exceedingly imperfect, probably even more so than that of liquids.

### *Radiation.*

When the hand is placed beneath a hot body suspended in the air, a distinct sensation of warmth is perceived, though from a considerable distance. This effect does not arise from the caloric being conveyed by means of a hot current; for all the heated particles have a uniform tendency to rise. Neither can it depend upon the conducting power of the air; since aerial substances possess that power in a very

low degree, while the sensation in the present case is excited almost on the instant. There is yet another mode by which caloric passes from one body into another; and as it takes place in all gases, and even in vacuo, it is inferred that the presence of a medium is not necessary to its passage. Their mode of transmission is called Radiation of Caloric, and the fluid so transmitted is called Radiant, or Radiated Caloric. We see, therefore, that a heated body suspended in the air cools, or is brought down to an equilibrium with surrounding bodies in three ways; first, by the conducting power of the air, whose influence is very trifling; secondly, by the mobility of the air in contact with it; and thirdly, by radiation.

Caloric is emitted from the surface of a hot body equally in all directions, and in right lines, like radii drawn from the centre to the circumference of a circle; so that a thermometer, placed at the same distance on any side, would stand at the same point, if the effects of the ascending current of hot air could be averted. The calorific rays, thus distributed, pass freely through a vacuum and the air, without being arrested by the latter or in any way affecting its temperature. When they fall upon the surface of a solid or liquid substance, they are either reflected from it, and thus receive a new direction, or they lose their radiant form altogether, and are absorbed. In the latter case, the temperature of the receiving substance is increased, in the former, it is unchanged.

The absorption of radiant caloric may be proved by placing a thermometer before the fire, or any other convenient source of heat, when the mercury will be seen to rise in the stem. It has been ascertained by accurate experiment, and may be demonstrated mathematically, that the intensity of effect diminishes according to the squares of the distance from the radiating point. Thus, the thermometer will indicate four times less heat at two inches, nine times less at three inches, and sixteen times less at four inches, than it did when it was only one inch from the heated substance.

The existence of a reflecting power may be shewn in a familiar manner, by standing at the side of a fire in such a position that its heat cannot reach the face directly, and then placing a large plate of tinned iron opposite the grate, and at such an inclination as permits the observer to see in it the reflection of the fire; as soon as it is brought to this inclination, a distinct impression of heat will be perceived upon the face. If a line be drawn from the source of heat to the point of a plane surface from which it is reflected, and a second line from that point to the spot where it produces its effect, the angles which these lines form with the reflecting plane are equal to each other, or, in philosophical language, the angle of incidence is equal to the angle of reflection. It is on account of this law that when a heated body is placed in the focus of a concave parabolic reflector, the diverging rays which strike upon it assume a parallel direction with respect to each other; and when these parallel rays impinge upon a second concave reflector, standing opposite to the former, they are made to converge, so as to meet in its focus, where a great degree of heat is developed. This fact, as applied to the sun's rays or red-hot bodies, has been long known. But it is a modern discovery that caloric emanates in invisible rays, which are subject to the same laws of reflection as those that are accompanied by light. The honour of establishing this fact by experiment is due to Messrs Saussure and Pictet of Geneva, who first proved it of an iron ball heated so as not to be luminous even in the

dark, and afterwards of a vessel of boiling water : but for a knowledge of the laws of radiation in general, we are indebted to the researches of Professor Leslie, published in his *Essay on Heat*.

Mr Leslie employed a hollow tin cube filled with hot water as the radiating substance. The rays proceeding from it were brought, by means of a concave mirror, into a focus, in which the bulb of a differential thermometer was placed. He found that certain substances radiated heat much more rapidly than others, and that the nature of the surface of a heated body had a singular influence upon its radiation. By adapting thin plates of different metals to the sides of the tin cube, and turning them successfully towards the mirror, he found a very variable effect produced upon the thermometer. A bright smooth polished metallic surface radiated caloric very imperfectly ; but if the surface was in the least degree dull or rough, the radiating power was immediately augmented. By covering the tin surface with a thin layer of isinglass, paper, wax, or resin, its power of radiation increased surprisingly. Metallic substances were observed to be the worst possible radiators, particularly such as are susceptible of a high polish, as gold, silver, tin, and brass ; but it is easy to make them radiate well by giving them the opposite properties, either by scratching their surface, or covering it with whiting, lamp-black, or any other convenient substance. It is commonly supposed that black surfaces radiate better than white ones, but I am not acquainted with any conclusive experiments in proof of it.

Mr Leslie next examined the power of different substances in reflecting caloric, and he soon arrived at the interesting conclusion, that those surfaces which radiate least reflect most powerfully. A polished plate of tin or brass is an excellent reflecting surface, but a bad radiating one ; remove the polish in any way, and you injure its reflecting in the same proportion as you improve its radiating power. His experiments, indeed, justify the conclusion, that the faculty of radiation is inversely as that of reflection.

There are only two modes by which calorific rays, falling upon a solid opaque body, can dispose of themselves ; they must either be reflected from it, or enter into its substance. In this case caloric is said to be absorbed. Now, it is manifest that those rays which are reflected cannot be absorbed ; and those which are not reflected, must be absorbed. Hence it follows that the absorption of caloric in the same body is inversely as its reflection ; and as the property of radiation is likewise inversely as that of reflection, the power of radiating and absorbing caloric must be proportional and equal.

In speaking of radiant caloric, it is necessary to distinguish calorific rays accompanied by light from those which are emitted by a non-luminous body, since their properties are not exactly similar. Thus, the absorption of luminous caloric, whether proceeding from the sun or a common fire, is very much influenced by colour ; it is most considerable in black and dark coloured surfaces, while it is much less in white ones. The influence of colour, on the contrary, over the absorption of non-luminous caloric is exceedingly slight ; it remains to be proved, indeed, whether any effect can fairly be attributed to this cause.

It may be asked, since radiant caloric passes without interruption through the air, whether it can pass in a similar manner through solid transparent media, as glass or rock-crystal. The only point of view under which this subject can be considered at present, is with respect



to radiant caloric emitted by a warm body which is not luminous. When a piece of clear glass is placed between such a body and a thermometer, the latter is not nearly so much affected as it would be were no screen interposed; and the glass itself becomes warm. These facts prove that at least the greater part of the calorific rays is intercepted by the glass. But the thermometer is affected to a certain degree; and the question is, by what means do the rays reach it? Professor Leslie contends that all the rays which fall upon the glass are absorbed by it, pass through its substance by its conducting power, and are then radiated from the other side of the glass towards the thermometer, an opinion which Dr Brewster has ably supported by an argument suggested by his optical researches. (Phil. Trans. for 1816, p. 106.) The experiments of Delaroche, on the contrary, (Biot. Tr. de Ph. v. 4.) lead to the conclusion that glass does transmit some calorific rays, the number of which, in relation to the quantity absorbed, is greater as the intensity of the heat increases; and the general result, obtained by that philosopher, agrees with some experiments which Dr Christison and I performed about two years ago on the same subject.

The facts that have been determined concerning the laws of radiant caloric have given rise to two ingenious modes of accounting for the tendency of bodies to acquire an equilibrium of temperature. This takes place, according to M. Pictet, in consequence of the hot body giving calorific rays to the surrounding colder ones till an equilibrium is established, at which moment the radiation ceases. Mr Prevost, on the contrary, contends that radiation goes on at all times, and from all bodies, whether their temperature is the same or different from those that surround them. According to this view, the temperature of a body falls whenever it radiates more caloric than it absorbs; its temperature is stationary when the quantities emitted and received are equal; and it becomes warm when the absorption exceeds the radiation. A hot body, surrounded by others colder than itself, is an example of the first case; the second happens when all the substances which are near one another have the same temperature; and the third occurs when a cold body is brought into a warm room.

Though neither of these theories have been proved to be true, and both of them have the merit of accounting for the phenomena of radiation, the preference is commonly given to the last. The theory of M. Prevost, is, indeed, more probable than that of M. Pictet. The chief argument in its favour is drawn from the close analogy between the laws of light and caloric. Luminous bodies certainly exchange rays with one another: a less intense light sends rays to one of greater intensity; and hence it may be inferred that an interchange of calorific rays takes place in a similar manner. Under this point of view, it is difficult to conceive how the radiation of one body should be influenced by the presence of another at a considerable distance from it.

This ingenious theory applies equally well to the experiments with the conjugate mirrors, as to the phenomena of ordinary radiation. If a metallic ball in the focus of one mirror, and a thermometer in that of the other, are both of the same temperature as the surrounding objects, (say at  $60^{\circ}$  F.) the thermometer remains stationary. It does indeed receive rays from the ball; but its temperature is not affected by them, because it gives back an equal number in return. If the ball is above  $60^{\circ}$  F. the thermometer begins to rise, because it now receives a greater number of rays than it gives out. If, on the contrary, the ball

is below  $60^{\circ}$  F. then the thermometer, being the warmer of the two bodies, emits more rays than it receives, and its temperature falls.

The same mode of reasoning accounts very happily for an experiment made by M. Pictet, the result of which at first appeared quite anomalous. He placed a piece of ice instead of the metallic ball in the focus of his mirror, and observed that the thermometer in the opposite focus immediately descended, but rose again as soon as the ice was removed. On replacing the ice in the focus, the thermometer again fell, and reascended when it was withdrawn. It was supposed by some philosophers that this experiment proved the existence of frigorific rays, whose property was to communicate coldness; whereas, all the preceding remarks are made on the supposition that cold is merely a negative quality arising from the diminution of caloric. If, indeed, the result of M. Pictet's experiment could not be explained on the latter supposition, we should be obliged to adopt the former; but as we are not driven to that alternative, it is nowise necessary to modify our views. In fact, as the thermometer gives more rays to the ice than it receives in return, it must necessarily become colder. It rises again when the ice is removed, because it then receives a number of caloric rays proceeding from the warmer surrounding objects, which were intercepted by the ice while it was in the focus. Whence it appears that the result of this experiment flows naturally out of M. Prevost's theory.

### *Effects of Caloric.*

The phenomena which accompany the passage of caloric into substances, are expansion, liquefaction, vaporization, incandescence and combustion; those that attend its escape from them are contraction, solidification of fluids, and condensation of vapour. But as these last are simply the converse of the former, all the effects of caloric upon matter may be arranged under the five heads which have been just mentioned. Incandescence and combustion will not however be considered at present, as it will be more convenient to treat of them in other parts of the work.

### *Expansion.*

One of the most remarkable properties of caloric is the repulsion which exists among its particles; hence it happens, that when this principle enters into a body, its first effect is to remove the integrant molecules of the substance to a greater distance from one another. The body therefore becomes less compact than before, occupies a greater space, or, in other words, expands. Now this effect of caloric is manifestly in opposition to cohesion—that force which tends to approximate the particles of matter, and which must be overcome before any expansion can ensue. One would expect, therefore, that a small addition of caloric would occasion a small expansion, and a greater addition of caloric a greater expansion; because in the last case the cohesion would be more overcome than in the former. It may be anticipated, also, that whenever caloric passes out of a body, the cohesion being now left to act freely, a contraction will necessarily follow; so that expansion is only a transient effect, occasioned solely by the accumulation of caloric. It follows, moreover, from this view, that caloric must produce the greatest expansion in those bodies,



whose cohesive power is least; and the inference is fully justified by observation. Thus the force of cohesion is greatest in solids, less in liquids, and least of all in aeriform substances; the expansion of solids is trifling, that of liquids much more considerable, and that of elastic fluids far greater.

It may be laid down as a rule, the reason of which is now obvious, that all bodies are expanded by caloric, and that the expansion of the same body increases with the quantity of caloric which enters it. But this law is a general one, only so long as the body under examination suffers no change in form or composition. If the caloric should produce one or both of these effects, then the reverse of expansion may ensue; not, however, as the direct consequence of an augmented temperature, but as the result of a change in form or composition.

In proof of the expansion of solids, we need only take the exact dimensions in length, breadth, and thickness of any substance when cold, and measure it again while strongly heated, when it will be found to have increased in every direction. A familiar demonstration of the fact may be afforded by adapting a ring to an iron rod, the former being just large enough to permit the latter to pass through it while cold. The rod is next heated, and will then no longer pass through the ring. This dilatation from heat and consequent contraction in cooling takes place with a force which appears to be irresistible.

The expansion of solids has engaged the attention of several experimenters, whose efforts have been chiefly directed towards ascertaining the exact quantity by which different substances are lengthened by a given increase of heat, and determining whether or not their expansion is equable at different temperatures. The Philosophical Transactions of London contain various dissertations on the subject by Ellicot, Smeaton, Troughton, and General Roy; and M. Biot, in his *Traité de Physique*, vol. i. has given the results of experiments performed with great care by Lavoisier and Laplace. Their experiments establish the following points: 1. Different solids do not expand to the same degree from equal additions of caloric. 2. A body which has been heated from the temperature of freezing to that of boiling water, and again allowed to cool to  $32^{\circ}$  F. recovers precisely the same volume which it possessed at first. 3. The dilatation of the more permanent or infusible solids is very uniform within certain limits; their expansion, for example, from the freezing point of water to  $122^{\circ}$  F., is equal to what takes place betwixt  $122^{\circ}$  and  $212^{\circ}$ . The subsequent researches of Dulong and Petit, (*Annales de Ch. et de Ph.* vol. vii.) prove that solids do not dilate uniformly at high temperatures, but expand in an increasing ratio; that is, the higher the temperature beyond  $212^{\circ}$  F. the greater the expansion for equal additions of caloric. It is manifest, indeed, from their experiments, that the rate of expansion is an increasing one even between  $32^{\circ}$  and  $212^{\circ}$ ; but the differences which exist within this small range are so inconsiderable as to escape observation, and therefore for all practical purposes may be disregarded.

The subjoined table includes the most interesting results of Lavoisier and Laplace. (Biot, vol. i. p. 158.)

<i>Names of Substances.</i>	<i>Elongation when heated from 32 to 212°.</i>
Glass tube without lead, a mean of three specimens . . . . .	*1-1115 of its length.
English flint glass . . . . .	1-1248
Copper . . . . .	1-581
Brass—mean of two specimens . . . . .	1-532
Soft iron forged . . . . .	1-819
Iron wire . . . . .	1-812
Untempered steel . . . . .	1-927
Tempered steel . . . . .	1-807
Lead . . . . .	1-351
Tin of India . . . . .	1-510
Tin of Falmouth . . . . .	1-462
Silver . . . . .	1-524
Gold—mean of three specimens . . . . .	1-662
Platinum, determined by Borda . . . . .	1-1167

Knowing the elongation of any substance for a given number of degrees of the thermometer, it is easy to calculate its total increase in bulk, by trebling the number which expresses its increase in length. Thus if a tube of flint glass elongates by 1-1248, when heated from the freezing to the boiling point of water, its cubic space will have increased by 3-128 or 1-416 of its former capacity.

The simplest method of proving the expansion of liquids is by putting a common thermometer, made with mercury or alcohol, into warm water, when the dilatation of the liquid will be shown by its ascent in the stem. The experiment is indeed illustrative of two other facts. It proves, first, that the dilatation is in proportion to the temperature; for if the thermometer is plunged into several portions of water heated to different degrees, the ascent will be greatest in the hottest water, and least in the coolest portions. It demonstrates, secondly, that liquids expand more than solids. The glass bulb of the thermometer is itself expanded by the hot water, and therefore is enabled to contain more mercury than before; but the mercury being dilated to a much greater extent, not only occupies the additional space in the bulb, but likewise rises in the stem. Its ascent marks the difference between its own dilatation and that of the glass.

Different liquids do not expand to the same degree from an equal increase of temperature. Alcohol expands much more than water, and water than mercury. From the frequency with which the latter is employed in philosophical experiments it is important to know the exact amount of its expansion. According to the experiments of Lavoisier and Laplace, its dilatation, in passing from the freezing to the boiling point of water, amounts to 100-5112 of its volume; but the result obtained by Dulong and Petit, who found it 100-5550, is probably still nearer the truth. Adopting the last estimate, this metal

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\* Throughout this work, in the American edition, all *separate* fractional expressions, such as  $\frac{1}{1115}$ ,  $\frac{1}{1248}$ ,  $\frac{1}{581}$ , &c. are represented in the following manner,—by placing the denominator in the same line with the numerator, preceded by a hyphen, thus; 1-1115, 1-1248, 1-581, &c. The diminutive size of the type used in printing this book renders the measure necessary.

dilates, for every degree of Fahrenheit's thermometer, 1-9990 of the bulk which it occupied at the temperature of 32° F. If the barometer, for instance, stands at 30 inches when the thermometer is at 32° F. we may calculate what its elevation ought to be when the latter is at 60°, or at any other temperature\*.

All experimenters agree that liquids expand in an increasing ratio, or that equal increments of caloric cause a greater dilatation at high than at low temperatures. Thus, if a fluid is heated from 32° to 122° it will not expand so much as it would do in being heated from 122° to 212°, though an equal number of degrees is added in both cases. In mercury the first expansion, according to Deluc, is to the second as 14 to 15; in olive oil as 13·4 to 15; in alcohol as 10·9 to 15; and in pure water as 4·7 to 15. Attempts have been made to discover a general law by which this progression is regulated, and Mr Dalton conceives that the expansion observes the ratio of the square of the temperature estimated from the point of congelation, or of greatest density; but this opinion is merely hypothetical, and has been shown by Dulong and Petit to be inconsistent with the facts established by their experiments.

There is a peculiarity in the effect of caloric upon the bulk of some fluids; namely, that at a certain temperature an increase of heat causes them to contract, and its diminution makes them expand. This singular exception to the general effect of caloric is only observable in those liquids which acquire an increase of bulk in passing from the liquid to the solid state, and is remarked only within a few degrees of temperature above their point of congelation. Water is a noted example of it. Ice, as every one knows, swims upon the surface of water, and therefore must be lighter than it, which is a convincing proof that water, at the moment of freezing, must expand. The increase is estimated at about 1-10th of its volume.

The most remarkable circumstance attending this expansion, is the prodigious force with which it is effected. Mr Boyle filled a brass tube, three inches in diameter, with water, and confined it by means of a moveable plug; the expansion, when it froze, took place with such violence as to push out the plug, though preserved in its situation by a weight equal to 74 pounds. The Florentine academicians burst a hollow brass globe, whose cavity was only an inch in diameter, by freezing the water with which it was filled; and it has been estimated

\* The general formula is as follows: let H be the height of the barometer when the thermometer is at 32° F.; H' its elevation at any temperature above 32°, and let T express the number of degrees of

Fahr. therm. above that point. Then  $H' = H \cdot \left(1 + \frac{T}{9990}\right)$ ; hence

$\frac{H'}{H} = 1 + \frac{T}{9990}$ ;  $H' \cdot 9990 = H \cdot (9990 + T)$ ; and  $H' = H \cdot \frac{9990 + T}{9990}$ ; or

if H is unknown, it may be calculated by the formula  $H = \frac{H' \cdot 9990}{9990 + T}$ .

For H and T in the first formula substitute their value, as stated in the text, and perform the calculation.  $H' = 30 \cdot \frac{9990 + 23}{9990} + 30 \cdot 084$ .

that the expansive power necessary to produce such an effect was equal to a pressure of 27,720 pounds weight.

But it is not merely during the act of congelation that water expands; for it begins to dilate considerably before it actually freezes. Various philosophers have observed this fact, and it may be rendered obvious to any one by the following experiment. Fill a flask, capable of holding three or four ounces, with water at the temperature of 60° F. and adapt a cork to it, through which passes a glass tube open at both ends, about the eighth of an inch wide, and ten inches long. After having filled the flask, insert the cork and tube, and pour a little water into the latter till the liquid rises to the middle of it. On immersing the flask into a mixture of pounded ice and salt, the water will fall in the tube, marking contraction; but in a short time an opposite movement will be perceived, indicating that dilatation is taking place, while the water within the flask is, at the same time, yielding caloric to the freezing mixture on the outside of it.

The inference deduced from this experiment was objected to by some philosophers, on the very obvious ground that the ascent of the water in the tube did not arise from any expansion in the liquid itself, but from a contraction of the flask, by which its capacity was diminished. In fact, this cause does operate to a certain extent, but it is by no means sufficient to account for the whole effect; and, accordingly, it has been proved by an elegant and decisive experiment of Dr Hope, that water does really expand previous to congelation. He found the greatest density of water to be at 39 and a half or 40 degrees of Fahrenheit's thermometer; that is, boiled water obeys the usual law till it has cooled to the temperature of 40° F. after which the abstraction of caloric produces an increase instead of a diminution of volume.

The cause of the expansion of water at the moment of freezing is attributed to a new and peculiar arrangement of its particles. Ice is in reality crystallized water, and, during its formation, the particles arrange themselves in ranks and lines, which cross each other at angles of 60° and 120°, and consequently occupy more space than when they were in a liquid state. This may be seen by examining the surface of water while freezing in a saucer. No very satisfactory reason can be assigned for the expansion which takes place previous to congelation. It is supposed, indeed, that the water begins to arrange itself in the order it will assume in the solid state before actually laying aside the liquid form; and this explanation is generally admitted, not so much because it has been proved to be true, but because no better one has been offered.

Water is not the only liquid which expands under reduction of temperature, as it is observed in a few others which assume a highly crystalline structure on becoming solid;—fused iron, antimony, zinc, and bismuth, are examples of it. Mercury is a remarkable instance of the reverse; for when it freezes it suffers a very great contraction.

As the particles of air and aeriform substances are not held together by cohesion, it follows that an increase of temperature must occasion a considerable dilatation of them; and, accordingly, they are found to dilate from equal additions of caloric much more than solids or liquids. Now, chemists are in the habit of estimating the quantity of the gases they employ in their experiments by measuring them, and since the volume occupied by any gas is so much influenced by temperature, it is essential to accuracy that a due correction be made for the variations arising from this cause; that we should know how much

dilatation is produced by each degree of the thermometer, whether the rate of expansion is uniform at all temperatures, and whether that ratio is the same in all gases.

This subject has been unsuccessfully investigated by several philosophers, who failed in their object chiefly because they neglected the precaution of drying the gases upon which they operated; but at last the law of dilatation was detected by Dalton and Gay-Lussac nearly at the same time. Mr Dalton's method of operating (*Manchester Memoirs*, vol. v.) was exceedingly simple. He filled with dry mercury a graduated tube, closed at one end and carefully dried; and then, plunging the open end of the tube into a mercurial trough, introduced a portion of dry air into it. After having marked the bulk and temperature of the air, he exposed it to a gradually increasing heat, the exact amount of which was regulated by a thermometer, and observed the dilatation occasioned by each increase of temperature. The apparatus of M. Gay-Lussac (*An. de Chimie*, v. 42.) was the same in principle, but more complicated, in consequence of the precautions he took to avoid every possible source of fallacy.

It is proved by the researches of these philosophers, that all gases undergo equal expansions by the same addition of caloric, supposing them placed under the same circumstances; so that it is sufficient to ascertain the law of expansion observed by any one gas, in order to know the law for all. Now, it appears from the experiments of Gay-Lussac, that 100 parts of air in being heated from  $32^{\circ}$  to  $212^{\circ}$  F. expand to 137.5 parts; the increase of bulk for 180 degrees is therefore 37.5, from which it may be calculated that a given quantity of dry air dilates to 1-480th of the volume it occupied at  $32^{\circ}$ , for every degree of Fahrenheit's thermometer. The result of Dalton's experiments corresponds very nearly with the foregoing.

This point being established, it is easy to ascertain what volume any given quantity of gas should occupy at any given temperature. Suppose a certain portion of gas occupies 20 measures of a graduated tube at  $32^{\circ}$ , it may be desirable to determine what would be its bulk at  $42^{\circ}$  F. For every degree of heat it has increased by 1-480th of its original volume, and therefore, as there has been an accession of ten degrees, the 20 measures will have dilated by 10-480ths. The expression will therefore be  $20 + 20 \cdot \frac{10}{480} = 20.416$ . It must not be forgotten that the volume which the gas occupies at  $32^{\circ}$  is a necessary element in all such calculations. Thus, having 20.416 measures of gas at  $42^{\circ}$  F. the corresponding bulk for  $52^{\circ}$  F. could not be calculated by the formula  $20.416 + 20.416 \cdot \frac{10}{480}$ ; the real expression is  $20.416 + 20 \cdot \frac{10}{480}$ , because the increase is only 10-480ths of the space occupied at  $32^{\circ}$  F. which is 20 measures\*. A similar remark applies to the formula for estimating the effect of heat on the height of the barometer.

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\* Very convenient general formulæ for such calculations may be thus deduced: Let  $P'$  be the volume of gas at any temperature above  $32^{\circ}$ ,  $T$  the number of degrees above that point, and  $P$  its volume at  $32^{\circ}$ . Then  $P' = P \cdot \left(1 + \frac{T}{480}\right)$ ; hence  $\frac{P'}{P} = 1 + \frac{T}{480}$ ;  $P' \cdot 480 = P \cdot (480 + T)$ ; and  $P' = P \cdot \frac{(480 + T)}{480}$



### On the Thermometer.

The influence of caloric over the bulk of bodies is better fitted for estimating a change in the quantity of that agent than any other of its properties; for substances not only expand more and more as the temperature increases, but return exactly to their original volume when the heat is withdrawn. The first attempt to measure the intensity of heat on this principle was made by Sanctorius, an Italian philosopher, in the 17th century, who is therefore considered to be the inventor of the thermometer. He employed a glass tube blown into a ball at one extremity and open at the other. After expelling a small quantity of the air from the ball by heating it gently, the open end was dipped into a coloured liquid, a portion of which ascended in the tube as the air within the ball contracted. Any variation of temperature would cause the surface of the liquid to rise or fall in the stem according as the air within the ball was either contracted by cold or dilated by heat. Sanctorius's thermometer was therefore made with air, a material peculiarly well adapted for the purpose, in reference to the uniformity of its expansion from equal increments of caloric. But there are two strong objections to its employment. For, in the first place, its dilatations and contractions are so great, that it will be inconvenient to measure them when the change of temperature is considerable; and secondly, its bulk is influenced by pressure, so that the instrument would be affected by variations of the barometer, though the temperature should be quite stationary.

For the reasons just stated, the common air thermometer is rarely

Or if  $P$  is unknown, it may be calculated by the formula  $P = \frac{P' \cdot 480}{480 + T}$ .

It frequently happens, in the employment of Fahrenheit's thermometer, that when  $P'$  for the above formula is known, it is not  $P$  itself which is wanted, but the volume of gas at some other temperature, as at  $60^\circ \text{F}$ . This value may be obtained without first calculating what  $P$  is. Let  $P'$ , for instance, be any known quantity of gas at a certain temperature; and let  $P''$  be the quantity sought at some other temperature, the degrees of which above  $32^\circ$  may be expressed by  $T'$ . Now

$$P' = \frac{(480 + T')}{480} \cdot P; \text{ but as } P \text{ is unknown, let its value be sub-}$$

stituted according to the above formula. Thus  $P'' =$

$$\left( \frac{480 + T'}{480} \right) \cdot \left( \frac{P' \cdot 480}{480 + T} \right); \text{ which gives } P'' = \frac{480^2 \cdot P' + 480 \cdot T' \cdot P'}{480^2 + 480 \cdot T} =$$

$$\frac{P' \cdot 480(480 + T')}{480(480 + T)} = \frac{P'(480 + T')}{480 + T}$$

Suppose, for example, a portion of gas occupies 100 divisions of a graduated tube at  $48^\circ \text{F}$ . how many will it fill at  $60^\circ \text{F}$ .? Here  $P' = 100$ ;  $T = 48 - 32$  or 16;  $T' = 60 - 32$ , or 28. The number sought,

$$\text{or the } P'' = \frac{100 \times 508}{496} = 102.42.$$



employed ; but the modification of it, described by Professor Leslie in his Essay on Heat, under the name of the Differential Thermometer, is entirely free from the last objection, and is admirably fitted for some special purposes. It consists of two thin glass balls joined together by a tube, bent twice at a right angle. Both balls contain air, but the greater part of the tube is filled with sulphuric acid coloured with carmine. It is obvious that this instrument cannot be affected by any change of temperature acting equally on both balls, for as long as the air within them expands or contracts to the same extent, the pressure on the opposite surface of the liquid, and consequently its position, will continue unchanged. Hence the differential thermometer stands at the same point, however different may be the temperature of the medium. But the slightest difference between the temperature of the two balls will instantly be detected, for the elasticity of the air on one side being now greater than that on the other, the liquid will retreat towards the ball whose temperature is lowest.

Solid substances are not better suited to the construction of a thermometer than gases ; for while the expansion of the latter is too great, that of the former is so small that it cannot be measured except by the adaptation of complicated machinery. Liquids, which expand more than the one and less than the other, are exempt from both extremes ; and, consequently, we must search there for a material with which to construct a thermometer. The principle of selection is plain. A material is required whose expansions are uniform, and whose boiling and freezing points are very remote from one another. Mercury fulfils these conditions better than any other liquid. No fluid can support a greater degree of heat without boiling than mercury, and none, except alcohol and ether, can endure a more intense cold without freezing. It has, besides, the additional advantage of being more sensible to the action of caloric than other liquids, while its dilatations between  $32^{\circ}$  and  $212^{\circ}$  are almost perfectly uniform. Strictly speaking, the same quantity of caloric does occasion a greater dilatation at high than at low temperatures, so that, like other fluids, it expands in an increasing ratio. But it is remarkable that this ratio, within the limits assigned, is exactly the same as that of glass ; and therefore, if contained in a glass tube, the increasing expansion of the vessel compensates for that of the mercury.

The first object in constructing a thermometer, is to select a tube with a very small bore, which is of the same diameter through its whole length ; and then, by melting the glass, to blow a small ball at one end of it. The mercury is introduced by rarefying the air within the ball, and then dipping the open end of the tube into that liquid. As the air cools and contracts, the mercury is forced up, entering the bulb to supply the place of the air which had been expelled from it. Only a part of the air, however, is removed by this means ; the remainder is driven out by the ebullition of the mercury.

Having thus contrived that the bulb and about one-third of the tube should be full of mercury, the next step is to seal the open end hermetically. This is done by heating the bulb till the mercury rises very near the summit, and then suddenly darting a fine pointed flame from a blow-pipe across the opening, so as to fuse the glass and close the aperture before the mercury has had time to recede from it.

The construction of a thermometer is now so far completed that it affords a means of ascertaining the comparative temperature of bodies ;

but it is deficient in one essential point, namely, the observations made with different instruments cannot be compared together. To effect this, the thermometer must be graduated, a process which consists of two parts. The first and most important, is to obtain two fixed points which shall be the same in every thermometer. The method now generally employed for this purpose was originally recommended by Sir Isaac Newton, and is founded on the fact, that when a thermometer is introduced into ice that is dissolving, or into water that is boiling, it constantly stands at the same elevations in all countries, provided there is a certain conformity of circumstances. The point of congelation is easily determined. The instrument is to be immersed in snow or pounded ice, which is liquefying in a moderately warm atmosphere, till the mercury becomes stationary. To fix the boiling point is a more delicate operation, since the temperature at which water boils is affected by various circumstances which will be more particularly mentioned hereafter. It is sufficient to state the general directions at present; that the water should be perfectly pure, free from any foreign particles, and not above an inch in depth,—the ebullition brisk, and conducted in a metallic vessel,—the vapour be allowed to escape freely,—and the barometer stand at 30 inches.

The second part of the process of graduation consists in dividing the interval between the freezing and boiling points of water, into any number of equal parts or degrees, which may be either marked on the tube itself, by means of a diamond, or first drawn upon a piece of paper, ivory or metal, and afterwards attached to the thermometer. The exact number of degrees into which the space is divided, is not very material, though it would be more convenient did all thermometers correspond in this respect. Unfortunately this is not the case. In Britain we use Fahrenheit's scale, while the continental philosophers employ either the centigrade, or that of Réaumur. The centigrade is the most convenient in practice: its boiling point is 100, that of melting snow is the zero, or beginning of the scale, and the interval is divided into 100 equal parts. The interval in the scale of Réaumur is divided into 80 parts, and in that of Fahrenheit into 180; but the zero of Fahrenheit is placed 32° below the temperature of melting snow, and on this account the point of ebullition is 212° F.

It is easy to reduce the temperature expressed by one thermometer to that of another, by knowing the relation which exists between their degrees. Thus, 180 is to 100 as 9 to 5, and to 80 as 9 to 4; so that nine degrees of Fahrenheit are equal to five of the centigrade, and four of Réaumur's thermometer. Fahrenheit's is therefore reduced to the centigrade scale, by multiplying by five, and dividing by nine, or to that of Réaumur, by multiplying by four instead of five. Either of these may be reduced to Fahrenheit by reversing the process; the multiplier is nine in both cases, and the divisor four in the one and five in the other. But it must be remembered in these reductions, that the zero of Fahrenheit's thermometer is 32 degrees lower than that of the centigrade or Réaumur, and a due allowance must be made for this circumstance. An example will best show how this is done. To reduce 212° F. to the centigrade, first abstract 32, which leaves 180; and this number multiplied by 5-9ths, gives the corresponding expression in the centigrade scale. Or to reduce 100° C. to Fahrenheit, multiply by 6-5ths, and then add 32.

The mercurial thermometer may be made to indicate temperatures which exceed 212°, or fall below zero, by continuing the degrees

above and below those points. But as mercury freezes at 40 degrees below zero, it cannot indicate temperatures below that point; and indeed the only liquid which can be used for such purposes is alcohol. Our means of estimating high degrees of heat are as yet very unsatisfactory. Mercury is preferable to any other liquid; but even its indications cannot be altogether relied on, because glass expands at temperatures beyond 212° F. in a more rapid ratio than mercury; and, therefore, from the proportionally greater capacity of the bulb, the apparent expansion of the metal is considerably less than its actual dilatation. No liquid can be employed for temperatures which exceed 600° F. since all of them are then either dissipated in vapour, or decomposed.

The instruments for measuring intense degrees of heat are called pyrometers, and must be formed either of solid or gaseous substances. The former alone have been hitherto employed, though it is probable that the latter, from the greater uniformity with which they expand, are better calculated for the purpose. The pyrometer invented by Mr Wedgewood is best known. It is founded on the property which clay possesses of contracting, when strongly heated, without returning to its former dimensions as it cools. The earth alumina, whether prepared by common chemical processes, or found more or less pure in the earth as clay, is always in a state of chemical combination with water. On heating it to redness, a part of the water is expelled; but some remains, which requires a very strong heat before it is dissipated; and in proportion as these last portions escape, the earth contracts. The contraction even continues after every trace of water has been removed, owing to a partial vitrification taking place, which tends to bring the particles of the clay into nearer proximity. The intensity of the heat may, therefore, in some measure be estimated by the degree of contraction which it has occasioned.

The apparatus consists of a metallic groove, 24 inches long, the sides of which converge, being half an inch wide above, and 3-tenths below. The clay, well washed, is made up into little cubes that fit the commencement of the groove, after having been heated to redness; and their subsequent contraction by heat is determined by allowing them to slide from the top of the groove downwards, till they arrive at a part of it through which they cannot pass. Mr Wedgewood divides the whole length of the groove into 240 degrees, each of which he supposes equal to 130° F. The zero of his scale corresponds to 1077 of Fahrenheit.

Wedgewood's pyrometer is little employed at present, because its indications cannot be relied on. Every observation requires a separate piece of clay, and the observer is never sure that the contraction of the second cube, from the same heat, will be exactly similar to the first; especially as it is difficult to procure specimens of the earth, whose composition is in every respect the same.

Other pyrometers have been proposed, which act on the usual principle of dilatation. They consist of a metallic bar, the elongation of which, from heat, is rendered sensible by an index being attached to one end, while the other is fixed. The experiments of Lavoisier and Laplace on the expansion of solids were made with such an apparatus, and Mr Daniell has lately described a similar one in the 11th volume of the London Journal of Science. These instruments are in general too complicated for common use; and, moreover, scientific men have

hitherto placed little confidence in them, in consequence of the irregularity with which solids expand at high temperatures.

Though the thermometer is one of our most valuable instruments of philosophical research, it must be confessed that the sum of information which it conveys is very small. It does indeed point out any difference in the temperature of two or more substances with great nicety ; but it does not indicate how much caloric any body contains. It does not follow, because the thermometer stands at the same elevation in any two bodies, that they contain equal quantities of caloric ; nor is it right to infer that the hottest of them possesses more of this principle than the colder. The thermometer can only recognize that peculiar state of matter with respect to caloric, which enables it to affect the senses with an impression of heat or cold ; that condition which is expressed by the word temperature. All we learn by this instrument, is whether the temperature of one body is greater or less than that of another ; and if there is a difference, it is expressed numerically, namely, by the degrees of the thermometer. But it must be remembered that these degrees are parts of an arbitrary scale, selected for convenience, without any reference whatever to the actual quantity of caloric present in bodies.

The justice of these remarks may be shown in a very simple manner. Take two glasses, one large, and the other small, and fill them with cold water from the same decanter. Now it is manifest that the water in the large glass must contain more caloric than that in the small one, and yet as their temperature is the same, the thermometer will stand at the same height in both. This observation naturally gives rise to an interesting question ; viz. do different kinds of substances, whose temperatures, as estimated by the thermometer, are the same, contain equal quantities of caloric ? For example, does a pound of iron contain as much caloric as a pound of water, or of mercury ? The foregoing observation will excite a suspicion that they do not contain equal quantities ; but the question has been determined in the following way. If equal quantities of water are mixed together, one portion being at  $100^{\circ}$  F., and the other at  $50^{\circ}$ , the mixture will have a temperature of  $75^{\circ}$ , or intermediate between the two ; that is, the 25 degrees which the warm water has lost, have just sufficed to raise the cold water by as many degrees. It is hence inferred that equal weights of water of the same temperature contain equal quantities of caloric ; and the same is found to be true of other bodies. But if equal weights, or equal bulks of different substances are used in the experiment, the result will be very different. Thus, if one pound of mercury at  $185^{\circ}$  F. is mixed with a pound of water at  $40^{\circ}$  F., the mixture will have a temperature of  $45^{\circ}$  F. only. The hot mercury has lost 140 degrees, all of which must have gone into the water ; yet its temperature is raised only five degrees. This experiment demonstrates that 28 times more caloric is required to raise the temperature of water through one or more degrees, than is required for heating an equal weight of mercury to the same extent ; from which it is inferred that the former contains 28 times more caloric than the latter. This result may be rendered more striking by reversing the experiment, by mixing a pound of water at  $185^{\circ}$  F., with a pound of mercury at  $40^{\circ}$ . The temperature of the mixture will be  $180^{\circ}$  F., the water having lost only five degrees, while the mercury has gained 140.

Similar experiments have been made by mixing water with a great many other substances ; and it is observed that different bodies always

require unequal quantities of caloric to heat them equally. The same quantity of caloric which heats a pound of water one degree, will heat an equal weight of Spermaceti oil two degrees, and, therefore, water is supposed to contain twice as much caloric as oil.

Dr Black was the first who noticed this remarkable difference, and he expressed it by the term capacity for caloric\*. The word capacity was probably suggested by the idea that the capacity of a body for caloric depends upon its capaciousness, or the distance between its particles, in consequence of which there is more room for caloric. And indeed at first view there appear sufficient grounds for this opinion; for it is observed, that very compact bodies have the smallest capacities for caloric, and that the capacity of the same substance increases as its density becomes less. But, as Dr Black himself pointed out, if this was the real cause of the difference, the capacity of bodies for caloric should be inversely as their density. Thus, since mercury is 13 times and a half denser than water, the capacity of the latter for caloric ought to be only 13 times and a half greater than the former, whereas it is 28 times as great. Oil occupies more space than an equal weight of water, and yet the capacity of the latter for caloric is double that of the former. The word capacity therefore is apt to excite a wrong notion, unless it is carefully borne in mind, that it is merely an expression of the fact without allusion to its cause; and to avoid the chance of error from this source, the term specific caloric has been substituted for it, and is now very generally employed.

It is certainly a singular and unexpected fact, that two substances of equal temperature should contain unequal quantities of caloric, and many attempts have been made to account for it. The explanation proposed by Dr Black is the following: He conceived that caloric exists under two opposite conditions; in one it is supposed to be in a state of chemical combination, lying hid as it were within a body, without evincing any signs of its presence; in the other, it is free and uncombined, passing readily from one substance to another, affecting our senses in its passage, determining the height of the thermometer, and in a word giving rise to all the phenomena which we attribute to this active principle.

Objections might easily be started against this ingenious conjecture; but it certainly has the merit of explaining phenomena more satisfactorily than any view that has been proposed in its place. We see by its means that two substances, from being in the same condition with respect to free caloric, will have the same temperature; and yet their actual quantities of caloric may be very different, in consequence of one of them containing more of that principle in a combined or latent state than the other. Perhaps it is better however to use the term sensible instead of free caloric, and insensible instead of combined or latent caloric; by which means the fact is equally well expressed, and the language of theory completely avoided.

It is of importance to know the specific caloric of bodies. The most convenient method of discovering it, is by mixing different substances together in the way just described, and observing the relative quantities of caloric requisite for heating them by the same number of de-

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\* Black's Lectures.



grees. The caloric required to heat equal quantities of water, spermaceti oil, and mercury by one degree, is in the ratio of 28, 14 and 1, and therefore their capacities for caloric are expressed by those numbers. Water is commonly one of the materials employed in such experiments, as it is customary to compare the capacity of other bodies with that of water.

This method was first suggested by Dr Black, and was afterwards practised to a great extent by Drs Crawford and Irvine\*. But the same knowledge may be obtained by reversing the process,—by noting the relative quantities of caloric which bodies give out in cooling; for if water requires 28 times more caloric than mercury to raise its temperature by one or more degrees, it must also lose 28 times as much when it cools. The calorimeter, invented and employed by Lavoisier and Laplace, acts on this principle. The apparatus consists of a wire cage, suspended in the centre of a metallic vessel so much larger than itself, that an interval is left between them, which is filled with fragments of ice. The mode of estimating the quantity of caloric which is emitted by a hot body placed in the wire cage, depends upon the fact, that ice cannot be heated beyond 32° F.; since every particle of caloric which then enters into it is employed in liquefying it, without in the least affecting its temperature. If, therefore, a flask of boiling water is put into the cage, it will gradually cool, the ice will continue at 32°, and a portion of ice-cold water will be formed; and the same change will happen when heated mercury, oil, or any other substance is substituted for the hot water. The sole difference will consist in the quantity of ice liquefied, which will be proportional to the caloric lost by those bodies while they cool; so that their capacity is determined merely by measuring the quantity of water produced by each of them. This is done by allowing the water, as it forms, to run out of the calorimeter by a tube fixed in the bottom of it, and carefully weighing the liquid which issues.

There is one obvious source of fallacy in this mode of operating, against which it is necessary to provide a remedy; namely, the ice not only receives heat from the substance in the central cage, but must also be warmed by the air of the apartment in which the experiment is conducted. This inconvenience is completely avoided by surrounding the whole apparatus by a larger metallic vessel of the same form as the smaller one, and of such a size that a certain space is left between them, which is to be filled with pounded ice or snow. No external heat can now penetrate to the inner vessel; because all the caloric derived from the apartment is absorbed by the outer one, and is employed, not in elevating its temperature, but in dissolving the pounded ice within it.

Notwithstanding this precaution, however, the accuracy of the calorimeter may fairly be questioned. That the results, obtained by it should be correct, it is essential that all the water which is produced should flow out and be collected. But it is strongly suspected that some of the water is apt to freeze again before it has had time to escape; and if this be true, as *a priori* is very probable, then the information given by the calorimeter must be rejected as useless.

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\* Crawford on Animal Heat, and Irvine's Chemical Essays.



The specific caloric of the gases may be determined in the same way as that of liquids and solids; but as the quantity of heat given out by them in cooling, even through a considerable number of degrees, is very small, the investigation is one of considerable difficulty. The following table contains the conclusions of Dr Crawford, and of Delaroche and Bérard. Equal weights of each substance are compared together, and the capacities are referred to water as unity.

	<i>Delaroche and Bérard.</i>	<i>Crawford.</i>
Water . . . . .	1.0000	1.0000
Air . . . . .	0.2669	1.7900
Hydrogen gas . . . . .	3.2936	21.4000
Carbonic acid gas . . . . .	0.2210	1.0454
Oxygen gas . . . . .	0.2361	4.7490
Nitrogen . . . . .	0.2754	0.7936
Nitrous oxide gas . . . . .	0.2369	
Olefiant gas . . . . .	0.4207	
Carbonic oxide gas . . . . .	0.2884	
Aqueous vapour . . . . .	0.8470	1.5500

The discrepancy in these results is a sufficient proof of the difficulty of the inquiry. Dr Crawford had determined by experiment, that solid bodies have a less capacity for caloric than liquids; and it follows, from the numbers contained in the preceding table, that gases in general are superior in this respect to liquids. It had also been observed that the specific caloric of a gas increased when it was dilated, and diminished when it suffered condensation. It seemed probable from this, that the capacity of the same body for caloric would increase when its density became less or its cohesion diminished, as when a solid liquefies, or a liquid is converted into vapour. These views were favoured by the experiments of Crawford, but completely overturned by those of Delaroche and Bérard; since, according to the first authority, the specific caloric of watery vapour is much greater than that of water, while, according to the second, it is considerably less.

The best way to form an opinion of the comparative accuracy of results which are so exceedingly discordant, is by direct appeal to experiment; but in the absence of such means, we must be guided by a comparison of the methods by which the experiments were conducted. Under this point of view, those of Delaroche and Bérard have a decided superiority. From being the most recent experimenters on the subject, they had all the experience of their predecessors to guide them; and their apparatus, though complicated and difficult to manage, was better suited to the object than that of Crawford. We can hardly hesitate, therefore, in giving a preference to the results of Delaroche and Bérard; and it is most probable that their numbers are fair approximations to the truth.

But these remarks apply only to the gases. The specific caloric of watery vapour cannot be regarded as known with the same degree of certainty: nor do Delaroche and Bérard themselves place much reliance on the accuracy of their results. This point then must be left to be decided by future observation; for the data which we at present possess cannot be trusted.

The facts hitherto determined concerning the specific caloric of bodies may be arranged under the five following heads.

1. Every substance has a specific caloric peculiar to itself; whence

it follows that a change of composition will be attended by a change of capacity for caloric.

2. A change of form, the composition remaining the same, is likewise attended by a change of capacity. It is increased when a solid liquefies, and diminished when a liquid passes into a solid. Thus the capacity of water in the solid state is 900, and in the liquid 1000. It was formerly supposed that the same substance has a greater specific caloric in the form of gas than when it is in a solid or liquid form; but the discrepancy above alluded to respecting the comparative specific caloric of water and watery vapour throws a doubt on this supposition which can be cleared away only by future and more accurate experiments.

3. It is certain that the specific caloric of all gases increases as their density diminishes, and *vice versa*\*. This being the case with the elastic fluids, it may reasonably be asked whether the same law does not extend to liquids and solids; whether water, for instance, at 32°, possesses the same specific caloric as at 212°, and through all the intermediate degrees. Drs Crawford and Irvine contended that it is permanent or nearly so, affirming that solids and liquids possess the same specific caloric at all temperatures, so long as they suffer no change of form or composition. Mr Dalton, on the contrary, (Chemical Philosophy, part i. p. 50) endeavours to show that the specific caloric of such bodies is greater in high than in low temperatures; and Petit and Dulong, in the essay already quoted, have proved it experimentally with respect to several of them. Thus the mean capacity of iron between

0° C	and	100° Cent	is	0.1098
0° C	.	200° C	.	0.1158
0° C	.	300° C	.	0.1218
0° C	.	350° C	.	0.1255

and the same is true of the substances contained in the following Table.

	<i>Mean capacity between 0° and 100° C</i>	<i>Mean capacity between 0° and 300° C</i>
Mercury	0.0330	0.0350
Zinc	0.0927	0.1015
Antimony	0.0507	0.0549
Silver	0.0557	0.0611
Copper	0.0949	0.1013
Platinum	0.0335	0.0335
Glass	0.1770	0.1900

4. Petit and Dulong have rendered it probable that the atoms of all simple substances have the same specific caloric. This opinion is founded on careful experiments, the results of which are contained in the following Table. (An. de Chimie et de Phys. vol. 10.)

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\* Delaroche and Bérard ascertained, that the capacity of gases for caloric does not increase in the same ratio as the diminution of density, but according to a less rapid progression. Thus, the specific caloric of any gas being 1, it is not 2 when its bulk is doubled, but between one and two.

	<i>Specific Caloric.</i>	<i>Relative Weights of Atoms.</i>	<i>Products of the weight of each Atom by the corresponding capacity.</i>
Bismuth	0.0288	13.30	0.3830
Lead	0.0293	12.95	0.3794
Gold	0.0298	12.43	0.3704
Platinum	0.0314	11.16	0.3740
Tin	0.0514	7.35	0.3779
Silver	0.0557	6.75	0.3759
Zinc	0.0927	4.03	0.3736
Tellúrium	0.0912	4.03	0.3675
Copper	0.0919	3.957	0.3755
Nickel	0.1035	3.69	0.3819
Iron	0.1100	3.392	0.3731
Cobalt	0.1498	2.46	0.3685
Sulphur	0.1880	2.011	0.3780

5. A change of capacity for caloric always occasions a change of temperature. An increase in the former is attended by a diminution of the latter; and a decrease in the former, by an increase of the latter. Thus, when air, confined within a flaccid bladder, is suddenly dilated by means of the air-pump, a thermometer placed in it will indicate the production of cold. On the contrary, when air is compressed, the corresponding diminution of its specific caloric gives rise to an increase of temperature; nay, so much heat is evolved when the compression is sudden and forcible, that tinder may be kindled by it. The explanation of these facts is obvious. In the first case, a quantity of caloric becomes insensible, which was previously in a sensible state; in the second, caloric is evolved, which was previously latent.

### *On Liquefaction.*

All bodies, hitherto known, are either solid, liquid, or gaseous; and the form they assume depends on the relative intensity of cohesion and repulsion. Should the repulsive force be comparatively feeble, the particles will adhere so firmly together, that they cannot move freely upon one another, thus constituting a solid. If cohesion is so far counteracted by repulsion, that the particles move on each other freely, a liquid is formed. And should the cohesive attraction be entirely overcome, so that the particles not only move freely on each other, but separate from one another to an indefinite extent, unless restrained by external pressure, an aeriform substance will be produced.

Now the property of repulsion is manifestly owing to caloric; and as it is easy within certain limits to increase or diminish the quantity of this principle in any substance, it follows that the form of bodies may be made to vary at pleasure; that is, by a sufficiently intense heat every solid may be converted into a fluid, and every fluid into the aeriform state. This inference is justified by experience so far, that it may safely be considered a general law. The converse ought also to be true; and, accordingly, the various gases, with the exception of three or four, have been condensed into liquids, and all liquids, except alcohol, have been solidified. The temperature at which liquefaction takes place is called the melting point, or point of fusion; and that at which liquids solidify, their point of congelation. Both these points

are different for different substances, but uniformly the same, *ceteris paribus*, in the same body.

The most important circumstance attending liquefaction, is the discovery of Dr Black, that a large quantity of caloric disappears, or becomes insensible to the thermometer during the process. If a pound of water at  $32^{\circ}$  be mixed with a pound of water at  $172^{\circ}$ , the temperature of the mixture will be intermediate between them, or  $102^{\circ}$ . But if a pound of water at  $172^{\circ}$  be added to a pound of ice at  $32^{\circ}$ , the ice will quickly dissolve, and on placing a thermometer in the mixture, it will be found to stand, not at  $102^{\circ}$ , but at  $32^{\circ}$ . In this experiment, the pound of hot water, which was originally at  $172^{\circ}$ , actually loses 140 degrees of caloric, all of which entered into the ice, and caused its liquefaction, but did not affect its temperature; and it follows, therefore, that a quantity of caloric becomes insensible during the melting of ice, sufficient to raise the temperature of an equal weight of water 140 degrees of Fahrenheit. This explains the well known fact, on which the graduation of the thermometer depends,—that the temperature of melting ice or snow never exceeds  $32^{\circ}$  F. All the caloric which is added becomes insensible, till the liquefaction is complete.

The loss of sensible caloric which attends liquefaction seems essentially necessary to the change, and for that reason is frequently called the caloric of fluidity. The actual quantity of caloric required for this purpose varies with the substance, as is proved by the following results obtained by Irvine. The degrees indicate the extent to which an equal weight of each material would have been heated by the caloric of fluidity which is proper to it.

	Caloric of Fluidity.
Sulphur . . . . .	$143^{\circ}.68$ F.
Spermaceti . . . . .	$145^{\circ}$ F.
Lead . . . . .	$162^{\circ}$
Bees-wax . . . . .	$175^{\circ}$
Zinc . . . . .	$493^{\circ}$
Tin . . . . .	$500^{\circ}$
Bismuth . . . . .	$550^{\circ}$

As so much heat disappears during liquefaction, it follows that caloric must be absorbed when a liquid passes into a solid. This may easily be proved. The temperature of water in the act of freezing never falls below  $32^{\circ}$  F. though it be exposed to an atmosphere in which the thermometer is at zero. It is obvious that the water can preserve its temperature in a medium so much colder than itself, only by the caloric which it loses being instantly supplied; and it is no less clear that the only source of supply is the caloric of fluidity. Further, if pure recently boiled water be cooled very slowly, and kept very tranquil, its temperature may be lowered to  $21^{\circ}$  F. without any ice being formed; but the least motion causes it to congeal suddenly; and in doing so, its temperature rises to  $32^{\circ}$  F.\*

The explanation which Dr Black gave of these phenomena, constitutes what is called his doctrine of latent heat. He considered that caloric loses its property of acting on the thermometer, in consequence of combining chemically with the solid substance, and that liquefaction is the result of this combination. Dr Irvine maintained a

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\* Sir Ch. Blagden, in Philos. Trans. for 1788.

different opinion. He admitted that liquefaction is produced by caloric; but denied that it is owing to any chemical combination. Observing that the capacity of a fluid for caloric was always greater than that of the solid from which it was produced, he ascribed the disappearance of caloric to the change in capacity which accompanies the change in form.

There is something unsatisfactory in both these doctrines. With respect to the first, there is no proof that caloric can unite chemically with ponderable matter at all. So little is known concerning the nature of caloric itself, that it is difficult to reason about its relation with other substances. It is most probable, indeed, that its presence in them is owing to chemical attraction; but even this point is not established with any certainty; much less are we entitled to say when such a combination does or does not take place.

Dr Irvine's view is in this respect less hypothetical than that of Dr Black; but it is nevertheless liable to objections. Liquids indeed are found to have a greater capacity for caloric than the solids which produced them, and this difference may account for heat disappearing during liquefaction. But it will soon be seen that the change of liquids into vapour renders insensible a much larger quantity of caloric than the conversion of solids into liquids, and yet it does not appear that the capacity of liquids is less than that of gaseous substances. According to the most recent experiments, those of Delaroche and Bérard, the specific caloric of watery vapour is considerably below that of water. If this is the fact, Dr Irvine's theory cannot stand.

After all, there appears to be a greater connexion between the cause of the different capacities for caloric and of Dr Black's theory of latent heat, than is usually admitted. They are different indeed, in so far as one is attended by a change of form and the other is not; but with respect to the disappearance of caloric, they are very analogous. To heat an equal weight of water and mercury by the same number of degrees, it is necessary to add 28 times as much heat to the water as to the mercury; which proves that a quantity of caloric becomes insensible to the thermometer when the temperature of water is raised by one degree, just as happens when ice is converted into water, or water into vapour. The two phenomena are so far identical; and consequently if an attempt be made to account for one of them, it is necessary to adopt some explanation that shall apply equally to the other. Now so far as I am aware, no plausible theory of this kind has been proposed; and therefore it is better to be satisfied with a simple statement of the fact.

The disappearance of sensible caloric in liquefaction is the basis of many artificial processes for producing cold. All of them are conducted on the principle of liquefying solid substances without the aid of heat. For the caloric of fluidity being then derived chiefly from that which had previously existed within the solid itself in a sensible state, the temperature necessarily falls. The degree of cold thus produced depends upon the quantity of caloric which disappears, and this again is dependent on the quantity of solid liquefied, and the rapidity of liquefaction.

The most common method of producing cold is by mixing together equal parts of snow and salt. The salt causes the snow to melt by reason of its affinity for water, and the water dissolves the salt, so that both of them become liquid. The cold thus generated is 32 degrees below the temperature of freezing water; that is, a thermometer



placed in the mixture would stand at zero. This is the way originally proposed by Fahrenheit for determining the commencement of his scale.

Any other substances which have a strong affinity for water may be substituted for the salt; and those have the greatest effect in producing cold whose affinity for that liquid is greatest, and which consequently produce the most rapid liquefaction. The crystallized muriate of lime, proposed by Lowitz, is by far the most convenient in practice. The salt may be made by dissolving marble in muriatic acid. The solution should be concentrated by evaporation, till upon letting a drop of it fall upon a saucer, it becomes a solid mass. It should then be withdrawn from the fire, and when cold be speedily reduced to a fine powder. From its extreme deliquescence it must be preserved in well-stopped vessels. The following table, from Mr Walker's paper in the Philosophical Transactions for 1801, contains the best proportions for producing an intense cold.

### *Frigorific Mixtures with Snow\*.*

Mixtures.	Thermom. Sinks.	Degree of Cold produced.
<i>Parts by Weight.</i>		
Muriate of Soda . . . 1	From any temperature.	to $-5^{\circ}$
Snow . . . . . 2		
Muriate of Soda . . . 2		to $-12^{\circ}$
Muriate of Ammonia . . 1		
Snow . . . . . 5	From any temperature.	to $-18^{\circ}$
Muriate of Soda . . . 10		
Muriate of Ammonia . . 5		to $-25^{\circ}$
Nitrate of Potash . . . 5		
Snow . . . . . 24	From any temperature.	to $-25^{\circ}$
Muriate of Soda . . . 5		
Nitrate of Ammonia . . 5		55 deg.
Snow . . . . . 12		
† Diluted Sulphuric Acid . 2	from $+32^{\circ}$ to $-23^{\circ}$	59
Snow . . . . . 3	from $+32^{\circ}$ to $-27^{\circ}$	
Concentrated Muriatic Acid . 5	from $+32^{\circ}$ to $-30^{\circ}$	62
Snow . . . . . 8	from $+32^{\circ}$ to $-40^{\circ}$	
Concentrated Nitrous Acid . 4	from $+32^{\circ}$ to $-50^{\circ}$	72
Snow . . . . . 7	from $+32^{\circ}$ to $-51^{\circ}$	
Muriate of Lime . . . 5		82
Snow . . . . . 4		
Crystallized Muriate of Lime . 3		83
Snow . . . . . 2		
Fused Potash . . . . 4		
Snow . . . . . 3		

\* The Snow should be freshly fallen, dry and uncompressed. If snow cannot be had, finely pounded ice may be substituted for it.

† Made of strong acid, diluted with half its weight of snow or distilled water.



But freezing mixtures may be made by the rapid solution of salts, without the use of snow or ice; and the following table, taken from Walker's paper in the Philos. Trans. for 1795, includes the most important of them. The salts must be finely powdered and dry.

Mixtures. <i>Parts by Weight</i>		Temperature Falls.	Degree of Cold produced.
Muriate of Ammonia	5	from $+50^{\circ}$ to $+10^{\circ}$	40 deg.
Nitrate of Potash	5		
Water	16		
Muriate of Ammonia	5	from $+50^{\circ}$ to $+4^{\circ}$	46
Nitrate of Potash	5		
Sulphate of Soda	8		
Water	16		
Nitrate of Ammonia	1	from $+50^{\circ}$ to $+4^{\circ}$	46
Water	1		
Nitrate of Ammonia	1	from $+50^{\circ}$ to $-7^{\circ}$	57
Carbonate of Soda	1		
Water	1		
Sulphate of Soda	3	from $+50^{\circ}$ to $-3^{\circ}$	53
Diluted Nitrous Acid*	2		
Sulphate of Soda	6	from $+50^{\circ}$ to $-10^{\circ}$	60
Muriate of Ammonia	4		
Nitrate of Potash	2		
Diluted Nitrous Acid	4		
Sulphate of Soda	6	from $+50^{\circ}$ to $-14^{\circ}$	64
Nitrate of Ammonia	5		
Diluted Nitrous Acid	4		
Phosphate of Soda	9	from $+50^{\circ}$ to $-12^{\circ}$	62
Diluted Nitrous Acid	4		
Phosphate of Soda	9	from $+50^{\circ}$ to $-21^{\circ}$	71
Nitrate of Ammonia	6		
Diluted Nitrous Acid	4		
Sulphate of Soda	8	from $+50^{\circ}$ to $-0^{\circ}$	50
Muriatic Acid	5		
Sulphate of Soda	5	from $+50^{\circ}$ to $+3^{\circ}$	47
Diluted Sulphuric Acid†	4		

These artificial processes for generating cold are much more effectual when the materials are previously cooled by immersion in other frigorific mixtures. One would at first suppose that an unlimited degree of cold might be thus produced; but it is found that when the difference between the mixture and the air becomes very great, caloric is so rapidly communicated from one to the other as to limit the reduction to a certain point. The greatest cold produced by Mr Walker, did not exceed 100 degrees below the zero of Fahrenheit.

\* Composed of fuming nitrous acid 2 parts in weight and one of water, the mixture being allowed to cool before being used.

† Composed of equal weights of strong acid and water, being allowed to cool before use.

Though it is unlikely that we shall ever succeed in depriving any substance of all its caloric, it is presumed that bodies do contain a certain definite quantity of this principle, and various attempts have been made to calculate the amount of it. The mode of conducting such a calculation may be shewn by the process of Dr Irvine. That ingenious chemist proceeded on the assumption, that the actual quantity of caloric in bodies must be proportional to their capacity, and that the capacity remained the same at all temperatures, provided no change of form ensued. Thus, as the capacity of ice is to that of water as 9 to 10, it follows that the one contains 1-10th more caloric than the other at the same temperature. Now Dr Black ascertained that this tenth, which is the caloric of fluidity, is equal to 140 degrees; whence it was inferred that water at 32° contains 10 times 140 or 1400 degrees of caloric.

To be satisfied that such calculations cannot be trusted, it is sufficient to know, that the estimates made by different chemists respecting the absolute quantity of caloric in water vary from 900 to nearly 8000\*. Besides even did the estimates agree with one another, the principle of the calculation would still be unsatisfactory; for, in the first place, there is no proof that the quantity of heat in bodies is in the ratio of their capacities; and, secondly, the assumption that the capacity of a body for caloric is the same at all temperatures, so long as it does not experience a change of form, has been proved to be wrong by the experiments of Petit and Dulong.

### *Vaporization.*

Aeriform substances are commonly divided into vapours and gases. The character of the former is, that they can be readily converted into liquids or solids, either by a moderate increase of pressure, the temperature at which they were formed remaining the same, or by a diminution of temperature, the pressure being unchanged. Gases, on the contrary, retain their elastic state more obstinately; they are always such at common temperatures, and cannot be made to change their form, except by being subjected to much greater pressure than they are naturally exposed to. Several of them, indeed, have hitherto resisted every effort to compress them into liquids.

Caloric appears to be the cause of vaporization, as well as of liquefaction, and it is a general opinion that a sufficiently intense heat would convert every liquid and solid into vapour. A considerable number of bodies, however, resist the strongest heat of our furnaces without vaporizing. These are said to be fixed in the fire; those which, under the same circumstances, are converted into vapour, are called volatile.

The disposition of different substances to form vapour is very different; and the difference depends doubtless on the relative power of cohesion with which they are endowed. Fluids are, in general, more easily vaporized than solids, as would be expected from the weaker cohesion of the former. Some solids, as arsenic and sal-ammoniac, pass at once into vapour without being liquefied; but most of them become liquid before assuming the elastic condition.

Vapours occupy more space than the substance from which they

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\* Dalton's New System of Chemical Philosophy.

were produced. According to the experiments of Gay-Lussac, water in passing into vapour expands to 1696 times its volume, alcohol to 659 times, and ether to 443 times. This shows that vapours differ in density. Watery vapour is lighter than air in the proportion of 1000 to 1604; or the density of air being 1000, that of watery vapour is 623. The vapour of alcohol, on the contrary, is half as heavy again as air; and that of ether is more than twice and a half as heavy. As alcohol boils at a lower temperature than water, and ether than alcohol, it was conceived that the density of vapours might be in the direct ratio of the volatility of the liquids which produced them. But Gay-Lussac has shewn that this law does not hold generally; for the carburet of sulphur boils at a higher temperature than ether, and nevertheless it forms the heaviest vapour.

The dilatation of vapours by heat was found by Gay-Lussac to follow the same law as gases, that is, for every degree of Fahrenheit, they increase by  $\frac{1}{480}$ th of the volume they occupied at  $32^{\circ}$ . But the law does not hold unless the quantity of vapour continues the same. If the increase of temperature cause a fresh portion of vapour to rise, then the expansion will be greater than  $\frac{1}{480}$ th, for each degree; because the heat not only dilates the vapour previously existing to the same extent as if it were a real gas, but augments its bulk by adding a fresh quantity of vapour. The contraction of a vapour on cooling will likewise deviate from the above law, whenever the cold converts any of it into a liquid—an effect which must happen, if the space had originally contained its maximum of vapour.

Vaporization is conveniently studied under two heads,—Ebullition and Evaporation. In the first, the production of vapour is so rapid that its escape gives rise to a visible commotion in the liquid; in the second, it passes off quietly and insensibly.

### *Ebullition.*

The temperature at which vapour rises with sufficient freedom for causing the phenomena of ebullition, is called the boiling point. The heat requisite for this effect varies with the nature of the fluid. Thus, sulphuric ether boils at  $96^{\circ}$  F., alcohol at  $173^{\circ}$ , and pure water at  $212^{\circ}$ ; while oil of turpentine must be raised to  $316^{\circ}$ , and mercury to  $660^{\circ}$  before either exhibits marks of ebullition. The boiling point of the same liquid is constant, so long as the necessary conditions are preserved; but it is liable to be affected by several circumstances. The nature of the vessel has some influence upon it. Thus, Gay-Lussac observed that pure water boils precisely at  $212^{\circ}$  in a metallic vessel, and at  $214^{\circ}$  in one of glass. It is likewise affected by the presence of foreign particles. The same accurate experimenter found, that when a few iron filings are thrown into water boiling in a glass vessel, its temperature quickly falls from  $214^{\circ}$  to  $212^{\circ}$ , and remains stationary at the last point. But the circumstance which has the greatest influence over the boiling point of fluids is variation of pressure. All bodies upon the earth are constantly exposed to considerable pressure; for the atmosphere itself presses with a force equivalent to a weight of 15 pounds on every square inch of surface. Liquids are exposed to this pressure as well as solids, and their tendency to take the form of vapour is very much counteracted by it. In fact, they cannot enter into ebullition at all, till their particles have acquired such an elastic force as enables them to overcome the pressure upon

their surfaces; that is, till they press against the atmosphere with the same force as the atmosphere against them. Now the atmospheric pressure is variable, and hence it follows that the boiling point of liquids must also vary.

The only time at which the pressure of the atmosphere is equal to a weight of 15 pounds on every square inch of surface, is when the barometer stands at 30 inches, and then only does water boil at  $212^{\circ}$  F. If the pressure be less, that is, if the barometer fall below 30 inches, then the boiling point of water, and every other liquid, will be lower than usual; or if the barometer rises above 30 inches, the temperature of ebullition will be proportionally increased. This is the reason why water boils at a lower temperature on the top of a hill than in the valley beneath it; for as the column of air diminishes in length as we ascend, its pressure must likewise suffer a proportional diminution. The ratio between the depression of the boiling point and the diminution of the atmospherical pressure is so exact, that it has been proposed as a method for determining the heights of mountains\*. An elevation of 530 feet makes a diminution of one degree of Fahrenheit.

The influence of the atmosphere over the point of ebullition is best shown by removing its pressure altogether. The late Professor Robison found that fluids boil in vacuo at a temperature 140 degrees lower than in the open air†. Thus water boils at  $72^{\circ}$  F. alcohol at  $33^{\circ}$  F. and ether at  $-44^{\circ}$  F. This proves that a liquid is not necessarily hot, because it boils. The heat of the hand is sufficient to make water boil in vacuo, as is exemplified by the common pulse-glass; and ether, under the same circumstances, will enter into ebullition, though its temperature is low enough for freezing mercury.

Water cannot be heated under common circumstances beyond  $212^{\circ}$  F., because it then acquires such an expansive force as enables it to overcome the atmospheric pressure, and to fly off in the form of vapour. But if subjected to sufficient pressure, it may be heated to any extent without boiling. This is best done by heating water while confined in a strong copper vessel, called Papin's Digester. A large quantity of vapour collects above the water, which checks the ebullition by the pressure it exerts upon the surface of the liquid. There is no limit to which water might not be heated in this way, provided the vessel is strong enough to confine the vapour; but the expansive force of steam under these circumstances is so enormous as to overcome the greatest resistance.

In estimating the power of steam, it should be remembered that vapour, if separated from the liquid which produced it, does not possess a greater elasticity than an equal quantity of air. If, for example, the digester was full of steam at  $212^{\circ}$ , no water in the liquid state being present, it may be heated to any degree, even to redness, without danger of bursting. But if water be present, then each addition of caloric causes a fresh portion of steam to rise, which adds its own elastic force to that of the vapour previously existing; and in consequence an excessive pressure is soon exerted against the inside of the vessel. Professor Robison (Brewster's edition of his works, p. 25) found that the tension of steam is equal to two atmospheres at  $244^{\circ}$  F., and to three at  $270^{\circ}$  F. The results of Mr Southern's experiments, given in the same volume, fix upon  $250.3^{\circ}$  F. as the temperature at

\* Wollaston in Phil. Trans. 1817.      † Black's Lectures, p. 151.

which steam has the force of two atmospheres, on  $293.4^{\circ}$  F. for four, and  $343.6^{\circ}$  F. for eight atmospheres.

The elasticity of steam is employed as a moving power in the steam-engine. The construction of this machine depends on two properties of steam, namely, the expansive force communicated to it by caloric, and its ready conversion into water by cold. The effect of both these properties is well shown by a little instrument devised by Dr Wollaston. It consists of a cylindrical glass tube, six inches long, nearly an inch wide, and blown out into a little ball at one end. A piston is accurately fitted to the cylinder, so as to move up and down the tube with freedom. When the piston is at the bottom of the tube, it is forced up by causing a portion of water, previously placed in the ball, to boil by means of a spirit-lamp. On dipping the ball into cold water, the steam which occupies the cylinder is suddenly condensed, and the piston is forced down by the pressure of the air above it. By the alternate application of heat and cold, the same movements are reproduced, and may be repeated for any length of time.

The moving power of the steam-engine is the same as in this apparatus. The only essential difference between them is in the mode of condensing the steam. In the steam-engine, the steam is condensed in a separate vessel, where there is a regular supply of cold water for the purpose. By this contrivance, which constitutes the great improvement of Watt, the temperature of the cylinder never falls below  $212^{\circ}$ .

The formation of vapour is attended, like liquefaction, with a loss of sensible caloric. This is proved by the well-known fact that the temperature of steam is precisely the same as that of the boiling water from which it rises; so that all the caloric which enters into the liquid is solely employed in converting a portion of it into vapour, without affecting the temperature of either in the slightest degree, provided the latter is permitted to escape with freedom. The caloric which then becomes latent, to use the language of Dr Black, is again set free when the vapour is condensed into water. The exact quantity of caloric absorbed, may therefore be ascertained by condensing the steam in cold water, and observing the rise of temperature occasioned by it. From the experiments of Dr Black and Mr Watt, conducted on this principle, it appears that steam of  $212^{\circ}$ , in being condensed into water of  $212^{\circ}$ , gives out as much caloric as would raise the temperature of an equal weight of water by 950 degrees, all of which had previously existed in the vapour without being sensible to a thermometer.

The latent heat of steam and several other vapours has been examined by Dr Ure\*, whose results are contained in the following table.

	<i>Latent Heat.</i>	
Vapour of water at its boiling point	.	967°
Alcohol	.	442
Ether	.	302.379
Petroleum	.	177.87
Oil of turpentine	.	177.87
Nitric acid	.	531.99
Liquid ammonia	.	837.28
Vinegar	.	875

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\* Philos. Trans. 1818.



The disappearance of caloric that accompanies vaporization was explained by Dr Black and Dr Irvine, in the way already mentioned under the head of liquefaction, and the objections then urged against each theory are likewise applicable on the present occasion.

### Evaporation.

Evaporation as well as ebullition consists in the formation of vapour, and the only assignable difference between them is, that the one takes place quietly, the other with the appearance of boiling. Evaporation takes place at common temperatures, as may be proved by exposing water in a shallow vessel to the air for a few days, when it will gradually diminish, and at last disappear entirely. Most fluids, if not all of them, are susceptible of this gradual dissipation; and it may also be observed in some solids, as for example in camphor. Evaporation is much more rapid in some fluids than in others, and it is always found that those liquids, whose boiling point is lowest, evaporate with the greatest rapidity. Thus alcohol, which boils at a lower temperature than water, evaporates also more freely; and ether, whose point of ebullition is yet lower than that of alcohol, evaporates still more rapidly.

The chief circumstances that influence the process of evaporation are extent of surface, and the state of the air as to temperature, dryness, stillness, and density.

1. Extent of surface. Evaporation proceeds only from the surface of fluids, and therefore, *ceteris paribus*, must depend upon the extent of surface exposed.

2. Temperature. The effect of heat in promoting evaporation may easily be shown by putting an equal quantity of water into two saucers, one of which is placed in a warm, the other in a cold situation. The former will be quite dry before the latter has suffered an appreciable diminution.

3. State of the air as to dryness or moisture. When water is covered by a stratum of dry air, the evaporation is rapid even when its temperature is low. Thus in some dry cold days in winter, the evaporation is exceedingly rapid; whereas it goes on very tardily, if the atmosphere contains much vapour, even though the air be very warm.

4. Evaporation is far slower in still air than in a current, and for an obvious reason. The air immediately in contact with the water soon becomes moist, and thus a check is put to evaporation. But if the air is removed from the surface of the water when it has become charged with vapour, and its place supplied with fresh dry air, then the evaporation continues without interruption.

5. Pressure over the surface of liquids has a remarkable influence over evaporation. This is easily proved by placing ether in the vacuum of an air pump, when vapour rises so abundantly as to produce ebullition.

As a large quantity of caloric passes from a sensible to an insensible state during the formation of vapour, it follows that cold should be generated by evaporation. A very simple experiment will prove it. If a few drops of ether be allowed to fall upon the hand, a strong sensation of cold will be excited during the evaporation; or if the bulb of a thermometer, covered with lint, be moistened with ether, the production of cold will be marked by the descent of the mercury. But to appreciate the degree of cold which may be produced by evaporation,

it is necessary to render it very rapid and abundant by artificial processes; and the best means of doing so, is by removing pressure from the surface of volatile liquids. Water placed under the exhausted receiver of an air-pump, evaporates with great rapidity, and so much cold is generated as would freeze the water, did the vapour continue to rise for some time with the same velocity. But the vapour itself soon fills the vacuum, and retards the evaporation by pressing upon the surface of the water. This difficulty may be avoided by putting under the receiver a substance, such as sulphuric acid, which has the property of absorbing watery vapour, and consequently of removing it as quickly as it forms. Such is the principle of Mr Leslie's method for freezing water by its own evaporation\*.

The action of the cryophorus, an ingenious contrivance of Dr Wollaston, depends on the same principle. It consists of two glass balls, perfectly free of air, and joined together by a tube. One of the balls contains a portion of distilled water, while the other parts of the instrument, which appear empty, are full of aqueous vapour, which checks the evaporation from the water by the pressure it exerts upon it. But when the empty ball is plunged into a freezing mixture, all the vapour within it is condensed; evaporation commences from the surface of the water in the other ball, and it is frozen in two or three minutes by the cold thus produced.

Liquids which evaporate more rapidly than water, cause a still greater reduction of temperature. The cold produced by the evaporation of ether in the vacuum of the air-pump, is so intense as to freeze mercury†.

Scientific men have differed concerning the cause of evaporation. It was once supposed to be owing to a chemical attraction between the air and water, and the idea is at first view plausible, since a certain degree of affinity does to all appearance exist between them. But it is nevertheless impossible to attribute the effect to this cause. For evaporation takes place equally in vacuo as in the air; nay, it is an established fact, that the atmosphere positively retards the process, and that one of the best means of accelerating it, is by removing the air altogether. The experiments of Mr Dalton prove that caloric is the true and only cause of the formation of vapour. He finds that the actual quantity of vapour which can exist in any given space, is dependent solely upon the temperature. If, for instance, a little water be put into a dry glass flask, a quantity of vapour will be formed proportional to the temperature. If a thermometer placed in it stands at 32° F. the flask will contain a very small quantity of vapour. At 40°, more vapour will exist in it; at 50° it will contain still more; and at 60°, the quantity will be still farther augmented. If, when the thermometer is at 60°, the temperature of the flask is suddenly reduced to 40°, then a certain portion of vapour will be converted into water; the quantity which retains the elastic form being precisely the same as when the temperature was originally at 40° F.

It matters not with regard to these changes, whether the flask is full of air, or altogether empty; for, in either case, it will eventually contain the same quantity of vapour, when the thermometer is at the same

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\* See Art. Cold in the Supplement to the *Encyclopædia Britannica*.

† See a paper printed by the late Dr Marcet in *Nicholson's Journal*, vol. xxxiv.

height. The only effect of a difference in this respect, is in the rapidity of evaporation. The flask, if previously empty, acquires its full compliment of vapour, or, in common language, becomes saturated with it, in an instant; whereas the presence of air affords a mechanical impediment to its passage from one part of the flask to another, and therefore an appreciable time elapses before the whole space is saturated.

Mr Dalton found that the tension or elasticity of vapour is always the same, however much the pressure may vary, so long as the temperature remains constant, and liquid enough is present for preserving the state of saturation proper to the temperature. If, for example, in a vessel containing a liquid, the space occupied by its vapour should suddenly dilate, the vapour it contains will dilate also, and consequently suffer a diminution of elastic force; but its tension will be quickly restored, because the liquid yields an additional quantity of vapour, proportional to the increase of space. Again, if the space be diminished, the temperature remaining constant, the tension of the confined vapour will still continue unchanged; because a quantity of it will be condensed proportional to the diminution of space, so that, in fact, the remaining space contains the very same quantity of vapour as it did originally. The same law holds good whether the vapour is pure or mixed with air or any other gas.

The elasticity of watery vapour at temperatures below  $212^{\circ}$  F. was carefully examined by Mr Dalton, (*Manchester Memoirs*, vol. v.); and his results, together with those since obtained by Dr Ure\*, are presented in a tabular form at the end of the volume. They were obtained by introducing a portion of water into the vacuum of a common barometer, and estimating the tension of its vapour by the extent to which it depressed the column of mercury at different temperatures. But Mr Dalton did not confine his researches to water; he extended them to the vapour of various liquids, as ether, alcohol, ammonia, and solution of muriate of lime, and inferred from them the following law:—That the force of vapour from all liquids is the same, at equal distances above or below the several temperatures at which they boil in the open air. Thus steam at  $200^{\circ}$ , F. has the same elasticity as the vapour of ether at  $85^{\circ}$ , the boiling point of the former being  $212^{\circ}$ , and of the latter  $97^{\circ}$ . Biot and Amédé Berthollet (*Biot, Traité de Ph.* vol. i. p. 282.) have found that this law applies exactly to many other liquids; but some experiments by Dr Ure on the oil of turpentine and petroleum, would lead to the conclusion that it is not universal.

The presence of vapour has a considerable influence over the bulk of gases; and as chemists often find it convenient to determine the quantity of gaseous substances by measure, it is important to estimate the effect thus produced, in order to make allowance for it. The mode by which a vapour acts is obvious. If a few drops of water are added to a portion of dry air, confined in a glass tube over mercury, the air will speedily become saturated with vapour, and must in consequence be increased in bulk. For the elastic power of the vapour being added to that previously exerted by the gas alone, the mixture will necessarily exert a stronger pressure upon the mercury that confines it, and will therefore occupy a greater space. It is equally clear that the degree of augmentation will depend on the temperature; for

\* *Philos. Trans.* 1818.

it is the temperature alone which determines the tension of the vapour.

As the elasticity of vapour is not at all affected by mere admixture with gases, it is easy to correct the fallacy to which its presence gives rise by means of the data furnished by the experiments of Dalton. The formula for the correction is thus deduced\*. Let  $n$  be the bulk of dry air or other gas expressed in the degrees of a graduated tube;  $p$  the tension of the dry air, equal to the atmospheric pressure;  $n'$  the bulk of the air when saturated with watery vapour,  $f$  the tension of that vapour.

It is a well-known law in physics that the elasticity of a gas is inversely as its volume; so that, when the dry air increases in bulk from  $n$  to  $n'$ , its elasticity diminishes in the ratio of  $n'$  to  $n$ . Hence its

elasticity ceases to be  $=p$ , but is expressed by  $\frac{pn}{n'}$ ;  $p$  is now  $=\frac{pn}{n'}$

+  $f$ ; that is, the elasticity of the dilated air, added to the elasticity of the vapour present, is equal to the pressure of the atmosphere. From this last equation are deduced the following values:  $pn + fn' = pn'$ ;

$$pn = pn' - fn'; \text{ and } n = \frac{n'(p-f)}{p}.$$

One example will suffice for showing the simplicity of this formula. Having 100 measures of air saturated with watery vapour at  $60^{\circ}$  F., the barometer standing at 30 inches, how many measures would the air occupy if quite dry?  $n' = 100$ ;  $p = 30$ ;  $f = 0.524$  according to Mr

Dalton's table. Hence  $n = \frac{100 \times (30 - 0.524)}{30} = \frac{100 \times 29.476}{30} =$

98.25 which is the answer required.

The presence of watery vapour in the atmosphere is owing to evaporation. All the accumulations of water upon the surface of the earth are subjected by its means to a natural distillation; the impurities with which they are impregnated remain behind, while the pure vapour ascends into the air, gives rise to a multitude of meteorological phenomena, and after a time descends again upon the earth as rain. As evaporation goes on to a certain extent even at low temperatures, it is probable that the atmosphere is never absolutely free of vapour.

The quantity of vapour present in the atmosphere is very variable, in consequence of the continual change of temperature to which the air is subject. But even when the temperature is the same, the quantity of vapour is still found to vary; for the air is not always in a state of saturation. At one time it is excessively dry, at another it is fully saturated; and at other times it varies between these extremes. This variable condition of the atmosphere as to saturation is ascertained by the hygrometer.

A great many hygrometers have been invented; but they may all be referred to two principles. The construction of the first kind of hygrometer is founded on the property possessed by some substances of expanding in a humid atmosphere, owing to a deposition of moisture within them; and of parting with it again to a dry air, and in consequence contracting. Almost all bodies have the power of attracting

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\* Biot, *Traité de Ph.* vol. i. p. 303.

moisture from the air, though in different proportions. A piece of glass or metal weighs sensibly less when carefully dried, than after exposure to a moist atmosphere; though neither of them is dilated, because the water cannot penetrate into their interior. Dilatation from the absorption of moisture appears to depend on a deposition of it within the texture of a body, the particles of which are moderately soft and yielding. The hygrometric property therefore belongs chiefly to organic substances, such as wood, the beard of corn, whalebone, hair and animal membranes. Of these, none is better than the human hair, which not only elongates freely from imbibing moisture, but, by reason of its elasticity, recovers its original length on drying.

The second kind of hygrometer points out the opposite states of dryness and moisture by the rapidity of evaporation. Water does not evaporate at all when the atmosphere is completely saturated with moisture; and the freedom with which it goes on at other times, is in proportion to the dryness of the air. The hygrometric condition of the air may be determined, therefore, by observing the rapidity of evaporation. The most convenient method of doing this, is by covering the bulb of a thermometer with a piece of silk or linen, moistening it with water, and exposing it to the air. The descent of the mercury, or the cold produced, will correspond to the quantity of vapour formed in a given time. Mr Leslie's hygrometer is of this kind.

A very elegant instrument for determining the dew-point, or the temperature at which dew is deposited, has been lately invented by Mr Jones of London, and Mr Coldstream of Leith. It consists of a common mercurial thermometer, with a bulb of black glass, the upper half of which is covered with muslin. When sulphuric ether is dropped upon the muslin, the temperature of the whole bulb sinks rapidly, and a deposition of dew soon becomes visible on the lower and exposed part of it. The degree indicated by the thermometer at that instant is the dew-point. (Phil. Trans. for 1826, and Edin. Phil. Journal, No. 17. p. 155.)

It is desirable, on some occasions, not merely to know the hygrometric condition of air or gases, but also to deprive them entirely of their vapour. This may be done to a great extent by exposing them to an intense cold; but the method now generally preferred is by bringing the moist gas in contact with some substance which has a powerful chemical attraction for water. Of these none is preferable to muriate of lime in a state of perfect dryness.

### *Constitution of the Gases with respect to Caloric.*

The experiments of Sir H. Davy and Mr Faraday on the liquefaction of gaseous substances appear to justify the opinion that gases are merely the vapours of extremely volatile liquids. These liquids, however, are so volatile, that their boiling point, under the atmospheric pressure, is lower than any natural temperature; and this is the reason why they are always found in the gaseous state. By subjecting them to great pressure, their elasticity is so far counteracted that they become liquid. But even when thus compressed, a very moderate heat is sufficient to make them boil; and on the removal of pressure they re-assume the elastic form, most of them with such violence as to cause a report like an explosion, and others with the appearance of brisk ebullition. An intense degree of cold is produced at the same time, in consequence of caloric passing from a sensible to an insensible state.



The process for condensing the gases (Philos. Trans. for 1823) consists in exposing them to the pressure of their own atmospheres. The materials for producing them are put into a strong glass tube, which is afterwards sealed hermetically, and bent in the middle. The gas is generated, if necessary, by the application of heat, and when the pressure becomes sufficiently great, the liquid forms and collects in the free end of the tube, which is kept cool to facilitate the condensation. Most of these experiments are attended with danger from the bursting of the tubes, against which the operator must protect himself by the use of a mask.

The pressure required to liquefy the gases is very variable, as will appear from the following table. The results were obtained by Mr Faraday.

Sulphurous acid gas	.	2 atmospheres at 45°F.
Sulphuretted hydrogen gas	.	17 . . . 50°F.
Carbonic acid gas	.	36 . . . 32°F.
Chlorine gas	.	4 . . . 60°F.
Nitrous oxide gas	.	50 . . . 45°F.
Cyanogen gas	.	3.6 . . . 45°F.
Ammoniacal gas	.	6.5 . . . 50°F.
Muriatic acid gas	.	40 . . . 50°F.

### *Sources of Caloric.*

The sources of caloric may be reduced to six. 1. The sun. 2. Combustion. 3. Electricity. 4. The bodies of animals during life. 5. Chemical action. 6. Mechanical action. All these means of procuring a supply of caloric, except the last, will be more conveniently considered in other parts of the work.

The mechanical method of exciting caloric is by friction and percussion. When parts of heavy machinery rub against one another, the heat excited, if the parts of contact are not well greased, is sufficient for kindling wood. The axle-tree of carriages has been burned from this cause, and the sides of ships are said to have taken fire by the rapid descent of the cable. Count Rumford has given an interesting account of the caloric excited in boring cannon, which was so abundant as to heat a considerable quantity of water to its boiling point. It appeared from his experiments that a body never ceases to give out heat by friction, however long the operation may be continued; and he inferred from this observation that caloric could not be a material substance, but was merely a property of matter. M. Pictet observed that solids alone can produce heat by friction, no elevation of temperature taking place from the mere agitation of fluids with one another. He found that the heat excited by friction is not in proportion to the hardness and elasticity of the bodies employed. On the contrary, a piece of brass rubbed with a piece of cedar wood produced more heat than when rubbed with another piece of metal; and the heat was still greater when two pieces of wood were employed.

## SECTION II.

*LIGHT.*

Light is similar to caloric in many of its properties. They are both emitted in the form of rays, traverse the air in straight lines, and are subject to the same laws of reflection. The intensity of each diminishes as the square of the distance from their source. They often accompany each other; and on some occasions seem to be actually converted into one another. It has been supposed, from this circumstance, that they might be modifications of the same agents, and though most persons regard them as independent principles, yet they are certainly allied in a way which is at present quite inexplicable.

There are two kinds of light, natural and artificial; the former proceeding from the sun and stars, the latter from bodies which are strongly heated. The light derived from these sources is so different, that it is necessary to speak of them separately.

The solar rays come to us either directly, as in the case of sunshine, or indirectly, in consequence of being diffused through the atmosphere, constituting day-light. They pass freely through some solid and liquid bodies, hence called transparent, such as glass, rock-crystal, water and many others, which, if clear and in moderately thin layers, intercept a portion of light that is quite inappreciable when compared to the quantity transmitted. Opaque bodies, on the contrary, intercept the rays entirely, absorbing some of them and reflecting others. In this respect, also, there is a close analogy between light and caloric: for every good reflector of the one, reflects the other also.

Though transparent substances permit the light to pass through them, they nevertheless exert a considerable influence upon it in its passage. All the rays which fall obliquely are refracted, that is, are made to deviate from their original direction. It was this property of transparent media which enabled Sir Isaac Newton to discover the compound nature of the solar light, and to resolve it into its constituent parts. The substance commonly employed for this purpose is a triangular piece of glass called the prism. Its action depends upon the different refrangibility of the seven-coloured rays which compose a colourless one. The violet ray suffers the greatest refraction, and the red the least; while the other colours of the rainbow lie between them, disposed in regular succession according to the degree of deviation which they have individually experienced. The coloured figure so produced is called the prismatic spectrum, which is always bounded by the violet ray on one side and by the red on the other.

The prismatic colours, according to the experiments of Sir W. Herschell, differ in their illuminating power. The orange possesses this property in a higher degree than the red; and the yellow rays illuminate objects still more perfectly. The maximum of illumination lies in the brightest yellow or palest green. The green itself is nearly equally bright with the yellow; but from the full deep green, the illuminating power decreases very sensibly. That of the blue is nearly equal to that of the red; the indigo has much less than the blue; and the violet is very deficient. (Phil. Trans. 1800.)

The solar rays, both direct and diffused, possess the property of exciting heat as well as light. This effect takes place only when the

rays are absorbed ; for the temperature of transparent substances through which they pass, or of opaque ones by which they are reflected, is not affected by them. Hence it happens that the burning glass and concave reflector are themselves nearly or quite cool at the very moment of producing a strong heat by collecting the sun's rays into a focus. The extreme coldness that prevails in the higher strata of the air arises from the same cause. The rays pass on unabsorbed through the atmosphere ; and the lower parts of it would be as cold as the upper, did they not receive caloric by communication from the earth.

The absorption of light is much influenced by the nature of the surface on which it falls ; and it is remarkable that those substances which absorb radiant non-luminous caloric most powerfully, are likewise the best absorbers of light. But there is one property of surfaces, namely, colour, which has a great influence over the absorption of light, but exceedingly little, if any, over that of pure radiant caloric. That dark-coloured substances acquire a higher temperature in the sunshine than light ones may be inferred from the general preference given to the latter as articles of dress during summer ; and this practice, founded on the experience of mankind, has been justified by direct experiment. Dr Hooke, and subsequently Dr Franklin, proved the fact by placing pieces of cloth of the same texture and size, but of different colours, upon snow, and allowing the sun's rays to fall upon them. The dark-coloured specimens always absorbed more caloric than the light ones, the snow beneath the former having melted to a greater extent than under the others ; and it was remarked that the effect was nearly in proportion to the depth of shade. Sir H. Davy has recently examined the subject, and arrived at the same conclusions.

The rays of the prismatic spectrum differ from one another in their heating power as well as in colour. Their difference in this respect was first noticed by Herschell, who was induced to direct his attention to the subject by the following circumstance. In viewing the sun by means of large telescopes through differently coloured darkening glasses, he sometimes felt a strong sensation of heat with very little light, and at other times he had a strong light with little heat,—differences which appeared to depend on the colour of the glasses which he used. This observation led to his celebrated researches on the heating power of the prismatic colours, which were published in the *Philosophical Transactions* for 1800.

The experiments were made by transmitting a solar beam through a prism, receiving the spectrum on a table, and placing the bulb of a very delicate thermometer successively in the different parts of it. While engaged in this inquiry, he observed not only that the red was the hottest ray, but that there was a point a little beyond the red, altogether out of the spectrum, where the thermometer stood higher than in the red itself. By repeating and varying the experiment, he discovered that the most intense heating power was always beyond the red ray, where there was no light at all ; and that the heat progressively diminished in passing from the red to the violet, where it was least. He hence inferred that there exists in the solar beam a distinct kind of ray, which causes heat but no light ; and that these rays, from being less refrangible than the luminous ones, deviate in a less degree from their original direction in passing through the prism.

All succeeding experiments confirm the statement of Sir W. Herschell that the prismatic colours have very different heating pow-

ers; but they are at variance with respect to the spot at which the heat is at a maximum. Some assert with Sir W. Herschell that it is beyond the red ray; while others, and in particular Professor Leslie, contend that it is in the red itself. This question has been decided by the recent observations of M. Seebeck. He found that the point of greatest heat was variable according to the kind of prism which was employed for refracting the rays. When he used a prism of fine flint glass, the greatest heat was constantly beyond the red. With a prism of crown glass, the greatest heat was in the red itself. When he employed a prism externally of glass, but containing water within, the maximum was neither in the red, nor beyond it, but in the yellow. It is difficult to account for these phenomena, except on the supposition that the different kinds of prisms differ in their power of refracting caloric. These experiments therefore confirm the opinion of Sir W. Herschell, that the sun-beam contains caloric rays, distinct from the luminous ones; and render it highly probable, that the heating effect imputed to the latter, is solely owing to the presence of the former.

It has been long known that the solar light is capable of producing powerful chemical changes. One of the most striking instances of it is its power of darkening the white muriate of silver, which takes place slowly in the diffused light of day, but in the course of one or two minutes by exposure to the sun-beam. This effect was once attributed to the influence of the luminous rays; but it appears from the observations of Ritter and Wollaston, that it is owing to the presence of certain rays that excite neither heat nor light, and which, from their peculiar agency, are termed chemical rays. It is found that the greatest chemical action is exerted just beyond the violet ray of the prismatic spectrum; that the spot next in energy is occupied by the violet ray itself; and that the property gradually diminishes as we advance to the green, beyond which it seems wholly wanting. It hence follows that the chemical rays are still more refrangible than the luminous ones, in consequence of which they are dispersed in part over the blue, indigo and violet, but in the greatest quantity at a point which is even beyond the latter.

The more refrangible rays of light possess the property of rendering steel or iron magnetic. This property was discovered in the violet ray by Dr Morichini of Rome; but as some experimentalists of eminence had repeated the experiments without success, the subject was involved in some degree of uncertainty. The fact, however, has been established by Mrs Somerville of London, who recently gave an account of her researches to the Royal Society. Sewing needles were rendered magnetic by exposure for two hours to the violet ray; and the magnetic property was communicated in a still shorter time, when the violet rays were concentrated by a lens. The indigo rays possess the magnetizing power almost to the same extent as the violet; and the blue and green possess the same power, though in a less degree. It is wanting in the yellow, orange and red. Needles were also rendered magnetic by the sun's rays, transmitted through green and blue glass.

The second kind of light is that which is emitted by substances when strongly heated. All bodies begin to emit light when caloric is accumulated within them in great quantity; and the appearance of glowing or shining, which they then assume, is called incandescence. The temperature at which solids in general begin to shine in the dark, is between 600° and 700° F.; but they do not appear luminous in

broad day-light, till they are heated to about  $1000^{\circ}$  F. The colour of incandescent bodies varies with the intensity of the heat. The first degree of luminousness is an obscure red. As the heat augments, the redness becomes more and more vivid, till at last it acquires a full red glow. Should the temperature still continue to increase, the character of the glow changes, and by degrees becomes white, shining with increasing brilliancy as the intensity of the heat augments. Liquids and gases likewise become incandescent when strongly heated; but a very high temperature is required to make a gas luminous, more than is sufficient for heating a solid body even to whiteness. The different kinds of flame, as of the fire, candles and gas light, are instances of incandescent gaseous matter.

All artificial lights are procured by the combustion or burning of inflammable matter. So large a quantity of caloric is evolved during the process that the body is made incandescent in the moment of being consumed. Those substances are preferred for the purposes of illumination that yield gaseous products when strongly heated, which, by becoming luminous while they burn, constitute flame. The light derived from such sources differs from the solar light in being accompanied by free radiant caloric similar to that emitted by a non-luminous heated body. The free radiant caloric may be separated by a screen of moderately thick glass; but the light so purified still heats any body that absorbs it, whence it would appear that it retains some calorific rays which, like those in the solar beam, accompany the luminous ones in their passage through solid transparent media\*. Terrestrial light has been supposed to contain no chemical rays. It is probable, however, that the attempts hitherto made to detect their presence, have failed rather from a want of delicacy in our tests than from their non-existence. This supposition is supported, or rather confirmed, by the chemical effects recently occasioned by phosphorescent lime. (*Annals of Philosophy*, June 1826.)

Light is emitted by some substances at common temperatures, giving rise to an appearance which is called phosphorescence. This phenomenon seems owing in some instances to a direct absorption of light which is afterwards slowly emitted. A composition made by heating to redness a mixture of calcined oyster shells and sulphur, known by the name of Canton's Phosphorus, possesses this property in a very remarkable degree. It shines so strongly for a few minutes after exposure to light, that when removed to a dark room the hour on a watch may be distinctly seen by it. After some time it ceases to be luminous, but it regains the property when exposed during a short interval to light. No chemical change attends the phenomenon.

Another kind of phosphorescence is observable in some bodies when they are strongly heated. A piece of marble, for example, heated to a degree which would only make other bodies red, emits a brilliant white light of such intensity that the eye cannot support the impression of it.

A third species of phosphorescence is observed in the bodies of some animals, either in the dead or living state. Some marine animals, and particularly fish, possess it in a remarkable degree. It may be witnessed in the body of the herring, which begins to phosphoresce a day or two after death, and before any visible sign of putrefaction has

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\* Mr Powell in *Phil. Trans.* for 1825.



set in. Sea-water is capable of dissolving the luminous matter; and it is probably from this cause that the waters of the ocean sometimes appear luminous at night when agitated. This appearance is also ascribed to the presence of certain animalcules, which, like the glow-worm of this country, or the fire-fly of the West Indies, are naturally phosphorescent.

It is sometimes of importance to measure the comparative intensities of light, and the instrument by which this is done is called a photometer. The only photometer which is employed for estimating the relative strength of the sun's light is that of Mr Leslie. It consists of his differential thermometer, with one ball made of black glass. The clear ball transmits all the luminous rays that fall upon it, and therefore its temperature is not affected by them: they are all absorbed, on the contrary, by the black ball, and by heating and expanding the air within it, cause the liquid to ascend in the opposite stem. The whole instrument is covered with a case of thin glass, the object of which is to prevent the balls from being affected by currents of cold air. The action of this photometer depends on the heat produced by the absorption of light. Mr Leslie conceives that light when absorbed is converted into heat; but according to the experiments already referred to, the effect must be attributed, not so much to the light itself, as to the absorption of the calorific rays which accompany it.

Mr Leslie recommends his photometer also for determining the relative intensities of artificial light, such as that emitted by candles, oil, or gas. This application of it differs from the foregoing, because the light proceeding from terrestrial sources contains caloric under two forms. One is analogous to that emitted by a body which is not luminous; the other is similar to that which accompanies the solar light. It is presumed that the first form of caloric will not prove a source of error: that these rays are wholly intercepted by the outer case of glass; or that should a few of them penetrate into the interior, they will be absorbed equally by both balls, and will therefore heat them to the same extent. It is probable that this reasoning is not wide of the truth; and, consequently, the photometer will give correct indications so far as regards the new element—non-luminous caloric. But it is not applicable to lights which differ in colour; for their heating power is out of all proportion to their light. Thus, the light emitted by burning cinders or red-hot iron, even after passing through glass, contains a quantity of calorific rays, which is out of all proportion to the luminous ones; and, consequently, they may and do produce a greater effect on the photometer than some lights whose illuminating powers are far greater.

The second kind of photometer is on a totally different principle. It determines the comparative strength of lights by a comparison of their shadows. This instrument was invented by Count Rumford, and is described by him in his *Essays*. It is susceptible of great accuracy when employed with the requisite care\*; but, like the foregoing, its indications cannot be trusted when there is much difference in the colour of the lights. In this case, the best mode of obtaining an approximative result, is by observing the distance from each light at which

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\* See an *Essay on the Construction of Coal Gas Burners, &c.* in the *Edinburgh Philosophical Journal* for 1825.

any given object, as a printed page, ceases to be distinctly visible. The illuminating power of the lights so compared is as the squares of the distance.

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## SECTION III.

### *ELECTRICITY.*

That some substances, such as glass, sealing-wax, and amber, acquire the property of attracting light bodies by friction is a fact which was known to the ancients. It appears to have been first noticed in amber, and hence the origin of the term Electricity, (from the Greek word *ηλεκτρον*, amber,) which was applied to the unknown cause of these phenomena. But no material progress was made in this branch of knowledge till the first half of the 18th century, when the discovery of new and important facts by Gray in this country, and Dufay in France, attracted general attention to the subject, and speedily acquired for it the regular form of a science.

Electricity is now very generally regarded, like the other imponderables, as a highly subtle elastic fluid, too light to affect our most delicate balances, moving with inconceivable velocity, and present in all bodies. It is one of the most active principles in nature. It is the cause of thunder and lightning; the phenomena of galvanism, and probably of magnetism, are produced by it; and it exerts such an influence over chemical changes, as to have given plausibility to the notion that it is the cause of them.

Though bodies always contain electricity, they do not always exhibit electrical phenomena. For this purpose they must be excited; and the best mode of exciting them is by friction. M. Dufay discovered that when two substances are rubbed together, both of them are excited, but are thrown into opposite electrical conditions. He conceived that there are two kinds of electricity, one of which he termed vitreous, the other resinous; the former being peculiar to glass when rubbed with a woollen cloth, and the latter to amber, sulphur, and resinous substances under similar treatment. He was led to this distinction by observing that two bodies which possess the same kind of electricity repel one another, and that substances in an opposite electrical condition attract each other.

These facts are explicable on the supposition that a repulsive power is exerted between the particles of the same kind of electricity, which causes an excited body to repel any other which is similarly electrified. The opposite electricities, on the contrary, are supposed to attract one another; and hence an attraction will be exerted between any two substances, one of which possesses vitreous, and the other resinous electricity. An unexcited body, according to this view, contains both electricities in a state of combination or neutralization, and cannot, therefore, exhibit any electrical attractions or repulsions. But friction disturbs this combination, or electric equilibrium as it is often called, causing the vitreous electricity to accumulate in one body and the resinous in the other. They are both, consequently, in an excited state,

and continue to be so till each recovers that kind of electricity which it had lost.

A different explanation was proposed by Dr Franklin, which is founded on the supposition that there is only one kind of electricity. When bodies contain their natural quantity of electricity, they do not manifest any electrical properties; but they are excited either by an increase or diminution in that quantity. On rubbing a piece of glass with a woollen cloth, the electrical condition of both substances is disturbed; the former acquires more, the other less than its natural quantity. These different states are expressed by the terms positive and negative, the first corresponding to the vitreous, the second to the resinous electricity of Dufay. The phenomena of electricity are explicable by both of these theories; but that of Dr Franklin is commonly preferred in this country.

The knowledge of the electrical attractions and repulsions affords an easy method of discovering when any substance is excited, as well as of distinguishing the kind of electricity which it possesses. A body is known to be in an excited state by its power of attracting light substances, or by causing two pith balls, suspended by silken threads, to repel one another when it is brought in contact with them. The strength of the electricity may be estimated by the extent of the divergence. Instruments of this kind are called Electroscopes and Electrometers; and one of the most sensible is that of Mr Bennet, which is made with two slips of gold leaf, and is hence called the Gold leaf Electrometer. If a pith ball, suspended by a silken thread, is rendered positive by being touched with an excited stick of glass, it will of course be repelled by presenting a positively electrified body to it; and, on the contrary, it will be attracted by one which is negative. In this way the kind of electricity may be readily determined.

Electricity may be excited in all solid substances by friction. This assertion seems at first view contrary to fact. It is well known that a metallic substance, if held in the hand, may be rubbed for any length of time without exhibiting the least sign of electricity; an observation which led to the division of bodies into such as may be excited by friction, and into those that give no sign of electrical excitement under the same circumstances. The former were called Electrics, the latter Non-electrics. But the distinction is not founded in nature. A metallic substance does not indeed exhibit any trace of electricity when rubbed in the same way as a piece of glass; but if, while it is rubbed with the dry fur of a cat, it is supported by a glass handle, it will be found to attract light bodies near it.

The difficulty and apparent impossibility of exciting metallic bodies, receives an explanation from the following facts. Philosophers have observed that the electric fluid passes with great facility along the surface of some substances, and with difficulty over that of others; and they have been led by this circumstance to the division of bodies into conductors and non-conductors of electricity. If an excited conductor, such as a metallic wire, be made to communicate with the earth at one of its extremities, the electricity will pass to it from the opposite end in an instant, even though it were several miles in length; so that when the equilibrium is disturbed, it will be at once restored along the whole wire, just as effectually as if every point of it had been in communication with the ground. But an excited stick of glass or resin is not affected in the same manner; for as electricity does not obtain a free passage along them, the equilibrium is restored in those parts only, which are actually touched. For this reason a

non-conductor of electricity, though held in the hand, may be readily excited; but a good conducting body cannot be brought into that state, unless it be insulated, that is, cut off from communication with the earth by means of some non-conductor.

To the class of conductors belong the metals, charcoal, plumbago, water, and most substances which contain water in its liquid state, such as animals and plants. To the list of non-conductors, belong glass, resins, sulphur, the diamond, dried wood, precious stones, silk, hair, and wool. Atmospheric air is also a non-conductor. If it were not so, no substance could retain its electricity when surrounded by it. Aqueous vapour suspended in the air injures the non-conducting property of the latter, and hence electrical experiments do not succeed so well when the air is charged with moisture as when it is dry. The presence of a little moisture communicates conducting properties to the worst non-conductor; and hence it is impossible to excite glass by rubbing it with a moist substance.

The construction of the electrical machine will now be intelligible. It consists of a large cylinder or plate of glass, which is made to revolve by means of a handle, and is pressed during its rotation by cushions stuffed with hair, so as to produce considerable friction. The positive electricity excited on the glass is conducted away by insulated bars of brass or other metal called the prime conductor, where it is collected in considerable quantity. The advantage of this arrangement is, that the electricity, spread over the whole surface of the prime conductor, passes at once to any substance which touches one point of it.

Friction is not the only exciter of electricity. The electric equilibrium is often disturbed by chemical action, or by the mere contact of two substances of a different kind, as when a plate of zinc is made to touch a plate of copper. The same body is sometimes excited by different parts of it being unequally heated. Electricity is developed during various natural processes as evaporation and the condensation of vapour, which may aid in accounting for certain electrical phenomena of the atmosphere. Another cause of excitement is proximity to an electrified body, which has a tendency to induce an electric state opposite to its own. Thus, an excited stick of sealing wax attracts light bodies in its vicinity, because, being itself negative, it occasions them to be positively electrified. When the inside of a glass bottle is rendered positive by contact with the prime conductor of the electrical machine, the outside of it, if in communication with the earth, becomes negative. On this depends the construction of the Leyden phial, which is merely a glass bottle or jar, coated to within three or four inches of its top both externally and internally with tin-foil. Its aperture is closed by some non-conducting substance, through the centre of which passes a metallic rod that communicates with the tin-foil in the inside of the jar. The phial is charged by holding the outside of it in the hand, or placing it on the ground, while the metallic rod is made to receive sparks from the prime conductor. If, in this charged state, the two surfaces are made to communicate by means of some conductor, the electric equilibrium will be instantly restored. An electrical battery is composed of a series of Leyden phials communicating with one another. The battery is charged and discharged in the same manner as a single phial.

The passage of electricity is frequently attended by the production of heat and light; an effect which invariably ensues when it meets

with an impediment to its progress, as in passing through a non-conductor. The most familiar example happens in its passage through the air, when it gives rise to a spark attended by a peculiar snapping noise, if in small quantity ; or to the phenomena of thunder and lightning when it takes place on a large scale. On the contrary, it passes along perfect conductors, such as the metals, without any perceptible warmth, or light, provided the extent of their surface is in proportion to the quantity of electricity to be transmitted by them ; but if the charge is too great in relation to the extent of the conducting surface, an intense degree of heat will be produced. Light and heat are likewise emitted at the moment the electric equilibrium is restored, as when the two surfaces of a charged Leyden phial are made to communicate by means of a good conductor.

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## SECTION IV.

### *GALVANISM.*

The science of galvanism owes its name and origin to the experiments on animal irritability made by Galvani about the year 1791. In the course of the investigation, he discovered the fact that muscular contractions are excited in the leg of a frog recently killed, when two metals, such as zinc and silver, one of which touches the crural nerve, and the other the muscles to which it is distributed, are brought into contact with one another. Galvani imagined that the phenomena were owing to electricity present in the muscles, and that the metals only served the purpose of a conductor. He conceived that the animal electricity originated in the brain, was distributed to every part of the system, and resided particularly in the muscles. He was of opinion that the different parts of each muscular fibril were in opposite states of electrical excitement, like the two surfaces of a charged Leyden phial, and that contractions took place whenever the electric equilibrium was restored. This he supposed to be effected during life through the medium of the nerves, and in his experiments by the intervention of metallic conductors.

The views of Galvani had several opponents, one of whom, the celebrated Volta, succeeded in pointing out their fallacy. Volta maintained that the electricity was excited by the contact of the metals ; that the animal substances merely acted as conductors in restoring the electric equilibrium at the moment of its being disturbed ; and that the contraction was produced by the stimulus arising from the passage of electricity along the nerves and muscular fibres. He proved that electricity was excited in the way he supposed, by bringing plates of different metals, as zinc and silver, in contact with one another, and examining their electrical state, at the moment of separation, by means of a delicate electrometer. For this purpose, it is necessary to insulate each of the metallic discs, by supporting them on a handle of glass or resin. On taking this precaution, it was found that both the metals were excited, the silver negatively, and the zinc positively.

As the quantity of electricity excited by any two metals is small,



Volta endeavoured to increase the effect by employing several pairs of metals, connecting them in such a manner that the electricity excited by each pair should be diffused through the whole series; and this attempt led him to the construction of the Voltaic pile, a description of which was published in the Philosophical Transactions for 1800. It consists of any number of pairs of zinc and copper, or zinc and silver plates, each pair being separated from the adjoining ones by pieces of cloth, nearly of the same size as the plates, and moistened in a saturated solution of salt. The relative position of the metals in each pair must be the same in the whole series; that is, if the copper is placed below the zinc in the first combination, the same order must be preserved in all the others. The pile is contained in a proper frame, formed of glass pillars, fixed into a piece of thick wood, which both supports and insulates it.

The apparatus so formed is in the same state of excitement as the insulated metallic discs after contact, and affects the electrometer and excites muscular contractions in a similar manner, but in a much greater degree. The opposite ends of the pile are also differently excited, the side which begins with a zinc plate being positive and the other negative; and hence, when they are made to communicate by means of a good conductor, electricity must pass from the one to the other, precisely as is supposed to happen in the discharge of a Leyden phial. But the apparatus is not thereby rendered inactive; for, as the conditions which originally excited it are still maintained, the equilibrium is no sooner restored than it is again disturbed, and therefore a continued current must pass from one end or pole to the other along the wire that connects them.

The Voltaic pile is now rarely employed, because we possess other modes of forming galvanic combinations which are far more powerful and convenient. The galvanic battery, proposed by Mr Cruickshank, consists of a trough of baked wood, about thirty inches long, in which are placed at equal distances fifty pairs of zinc and copper plates previously soldered together, and so arranged that the same metal shall always be on the same side. Each pair is fixed in a groove cut in the sides and bottom of the box, the points of junction being made watertight by cement. The apparatus thus constructed is always ready for use, and is brought into action by filling the cells left between the pairs of plates with some convenient solution, which serves the same purpose as the moistened cloth in the pile of Volta.

Other modes of construction are now in use which facilitate the employment of it, and increase its energy. The trough, made either of baked wood or glazed earthen ware, is divided into partitions of the same material. Each cell contains a plate of zinc and another of copper, which do not touch each other, but communicate merely through the medium of the fluid in which they are immersed. The zinc plate of one cell is connected with the copper of the adjoining one by means of a slip of copper. All the plates are attached to a piece of wood, and may thus be introduced into the liquid of the trough, or removed from it at pleasure. This method was suggested by the *Couronne des Tasses* of Volta, an arrangement which was described by him, together with his pile, in the paper already alluded to. An additional improvement was suggested by Dr Wollaston, (see Mr Children's paper in the Philos. Trans. for 1815), who recommends that each cell should contain one zinc and two copper plates, so that both surfaces of the first metal are opposed to one of the second. In

consequence of this arrangement, the plates of copper communicate with each other, and the zinc between them with the copper of the adjoining cell. An increase of one half the power is obtained by this method.

The size and number of the plates may be varied at pleasure. The largest battery ever made is that of Mr Children, described in the paper above referred to, the plates of which are six feet long, and two feet eight inches broad. The common and most convenient size for the plates is four or six inches square; and when great power is required, a number of different batteries are united by establishing a metallic communication between the positive pole of one battery and the negative pole of the adjoining one. The great battery of the Royal Institution is composed of 2000 pairs of plates, each plate having 22 square inches of surface. It was by this that Sir H. Davy was enabled to effect the decomposition and determine the constitution of the alkalis, a discovery which has at once extended so much the bounds of chemical science, and conferred immortal honour on the name of the discoverer.

The action of the galvanic trough is always attended by chemical changes between the liquid of the cells and one of the metals with which it is in contact. It has indeed been maintained by one of the most profound philosophers of the age, that such changes are essential to the production of galvanism; and it is certain that the action of the pile or battery is neither permanent nor energetic without their occurrence. The energy of a galvanic trough is, in fact, proportional to the degree of chemical action which takes place. When pure water is put into the cells, the action is feeble, because the accompanying chemical changes are feeble; but still the zinc is observed to rust more rapidly than it would do, were it not in contact with copper. A solution of some saline substance increases the energy of the pile; and the zinc is also found to oxidize more rapidly than in the first case. An acid fluid corrodes the metal with still greater rapidity, and augments the activity of the battery in the same proportion.

In constructing a galvanic battery, each member of the series must consist either of one imperfect and two perfect conductors, or of one perfect and two imperfect. The annexed tables, from Sir H. Davy's *Elements of Chemical Philosophy*, contain some series of both kinds, arranged in the order of their powers; the substance which is most active being named first in each column. Among the good or perfect conductors are the metals and charcoal. The imperfect conductors are water, and saline or acid solutions.

*Table of some electrical arrangements, which, by combination, form Voltaic batteries, composed of two conductors and one imperfect conductor.*

Zinc		Solutions of Nitric Acid	
Iron		Muriatic Acid	
Tin		Sulphuric Acid	
Lead		Sal-Ammoniac	
Copper		Nitre	
Silver		other Neutral Salts.	
Gold			
Platina			
Charcoal			

Each of these is the positive pole to all the metals below it, and negative with respect to the metals above it in the column.

*Table of some electrical arrangements, consisting of one conductor, and two imperfect conductors.*

Solution of Sulphur and Potash Potash Soda	Copper	Nitric Acid
	Silver	Sulphuric Acid
	Lead	Muriatic Acid
	Tin	Any solution containing Acid.
	Zinc	
	other Metals	
	Charcoal	

In all combinations in which the fluids act chemically by affording oxygen, the positive pole is always attached to the metal which has the strongest affinity for oxygen; but when the fluid menstrea afford sulphur to the metals, the metal which has the strongest affinity for sulphur will be positive. Thus, in a series of copper and iron plates introduced into a porcelain trough, the cells of which are filled with water or acid solutions, the iron is positive, and the copper negative; but when the cells are filled with solution of sulphur and potash, the copper is positive, and the iron negative.

In all combinations in which one metal is concerned, the surface opposite to the acid is negative, and that in contact with the solution of alkali and sulphur, or of alkali, is positive. (Elements of Chemical Philosophy.)

The more remarkable effects of the galvanic battery may be conveniently considered under 4 heads. 1st, Its electrical phenomena; 2d, its chemical agency; 3d, its power of igniting the metals; and 4th, its action on the magnet.

I. A galvanic battery may be made to produce all the phenomena occasioned by the common electrical machine. It will cause the gold leaves of the electrometer to diverge, and a Leyden phial, or even an electrical battery, may be charged by it. When conductors, connected with the opposite poles of an active galvanic trough, are brought near each other, a spark is seen to pass between them; and on establishing the communication by means of the hands, previously moistened, a distinct shock is perceived, though of a peculiar nature. These properties naturally gave rise to the belief, that the agent or power excited by the Voltaic apparatus, is identical with that which is called into activity by the electrical machine, and the arguments in favour of this opinion seem quite satisfactory. For not only may all the common electrical experiments be performed by means of galvanism; but it has been shown by Dr Wollaston, (Phil. Tr. for 1801) that all the chemical effects of the galvanic battery may be produced by electricity.

For producing intense heat and light, a battery composed of large plates is preferable. Small ones, on the contrary, should be employed when the object is to give shocks, to charge a Leyden phial, or affect an electrometer; for the power of a battery, in this point of view, depends upon the number rather than on the size of its plates. The apparatus should be excited by an acid solution when it is wished to draw sparks or produce a shock; but for charging a Leyden phial, or affecting the electrometer, the cells should be filled by preference with water only\*.

\* Singer on Electricity, p. 336.

II. The chemical agency of the Voltaic apparatus, to which chemists are indebted for their most powerful instrument of analysis, was discovered by Messrs Carlisle and Nicholson, soon after the invention was made known in this country. The substance first decomposed by it was water. When two gold or platinum wires are connected with the opposite poles of a battery, and their free extremities are plunged into the same cup of water, but without touching each other, hydrogen gas is disengaged at the negative wire, and oxygen at the positive side. By collecting the gases in separate tubes as they escape, they are found to be quite pure, and in the exact proportion of two measures of hydrogen to one of oxygen. When wires of a more oxidable metal are employed, the result is somewhat different. The hydrogen gas appears as usual at the negative pole; but the oxygen, instead of escaping, combines with the metal, and converts it into an oxide.

This important discovery led many able experimenters to make similar trials. Other compound bodies, such as acids and salts, were exposed to the action of galvanism, and all of them were decomposed without exception, one of their elements appearing at one side of the battery, and the other at its opposite extremity. An exact uniformity in the circumstances attending the decomposition was also remarked. Thus, in decomposing water or other compounds, the same kind of body was always disengaged at the same side of the battery. The metals, inflammable substances in general, the alkalies, earths, and the oxides of the common metals, were found at the negative pole; while oxygen, chlorine, and the acids, went over to the positive surface.

In performing some of these experiments, Sir H. Davy observed, that if the conducting wires were plunged into separate vessels of water, which were made to communicate by some moist fibres of cotton or amianthus, the two gases were still disengaged in their usual order, the hydrogen in one vessel, and the oxygen in the other, just as if the wires had been dipped into the same portion of that liquid. This singular fact, and another of the like kind observed by Hisinger and Berzelius, induced him to operate in the same way with other compounds, and thus gave rise to his celebrated experiments on the transfer of chemical substances from one vessel to another, detailed in the *Philosophical Transactions* for 1807. Two agate cups, N and P, were employed in them, the first communicating with the negative, the second with the positive pole of the battery, and connected together by moistened amianthus. On putting a solution of sulphate of potash or soda into N, and distilled water into P, the acid very soon passed over to the latter, while the liquid in the former, which was at first neutral, became distinctly alkaline. The process was reversed by placing the saline solution in P, and the distilled water in N, when the alkali went over to the negative cup, leaving pure acid in the positive. That the acid in the first experiment, and the base in the second, actually passed along the amianthus, was obvious; for, on one occasion, when nitrate of silver was substituted for the sulphate of potash, the amianthus leading to N, was coated with a film of metal. A similar transfer may be effected by putting distilled water into N and P, and a saline solution in a third cup placed between the two others, and connected with each of them by moistened amianthus. In a short time the acid of the salt appears in P, and the alkali in N.

The galvanic action not only separates the elements of compound bodies, but suspends the operation of affinity so entirely as to enable

an acid to pass through an alkaline solution, or an alkali through water containing a free acid, without combination taking place between them. The three cups being arranged as in the last experiment, Sir H. Davy put a solution of sulphate of potash in N, pure water in P, and a weak solution of ammonia in the intermediate cup, so that no sulphuric acid could find its way to the distilled water in P, without passing through the ammoniacal liquid on its passage. A battery composed of 150 pairs of 4-inch plates was set in action, and in five minutes free acid appeared at the positive pole. Muratic and nitric acids were in like manner made to pass through strong alkaline solutions; and, on reversing the experiment, alkalies were transmitted directly through acid liquids without entering into combination with them.

The analogy between the preceding phenomena and the attractions and repulsions exerted by ordinary electricity is too close to escape observation. If an acid or an alkali pass from one vessel to another in opposition to gravity and chemical affinity, it is clear that it must arise from its being under the influence of a still stronger attraction; and the only power to which such an effect can in the present case be attributed, is electricity. Now, in all instances of common electrical attraction, the bodies attract one another in consequence of being in opposite states of excitement; and, in like manner, the tendency of acids towards the zinc, and of alkalies towards the copper extremity of the Voltaic apparatus, can be accounted for, consistently with our present knowledge, only on the supposition that the former are negatively, and the latter positively electric, at the moment of being separated from one another. To explain how the elements of compounds may be in such a state, Sir H. Davy conceives that all bodies possess natural electric energies, which are inherent in them whether they are in a state of combination or not; and that some of them, such as oxygen, chlorine, iodine, and acids in general, are naturally negative, while hydrogen, metals, and metallic oxides, are naturally positive. The facts on which this opinion is founded are very remarkable. On bringing dry acids in contact with a metallic plate properly insulated, it was found, after separation, that the former were excited with negative and the latter with positive electricity. On touching the same metal with earthy and alkaline substances, the latter became positive and the former negative. It might hence be expected that acid and alkaline bodies would exhibit opposite electrical energies if directly compared together; and this was proved by the contact of lime with crystals of oxalic acid, when the lime exhibited the character of positive, and the acid of negative electricity. It appears, therefore, that the electric equilibrium of bodies which have a strong affinity for each other, is readily disturbed by mere contact; and Sir H. Davy conceives that the opposite energies which are then manifested are inherent in them at all times.

The author of this ingenious view not only applies it to explain the chemical agency of the Voltaic apparatus, but has founded upon it an hypothesis concerning the nature of affinity. He suggests that chemical attraction and the phenomena of electricity are owing to the same cause, that the same power which communicates attractive and repellent properties to masses of matter, will, when acting upon the ultimate particles of different bodies, induce them either to separate or combine, according as their natural electric energies are the same or different. Thus, since hydrogen is naturally positive and oxygen ne-



gative, they will have a tendency to enter into combination ; but if the oxygen could be brought by any artificial means into the same electric condition as the hydrogen, no combination would ensue between them ; or, if already combined, they would instantly separate. The decomposition of water would also be affected by the presence of a third substance whose negative energy exceeds that of oxygen. A Voltaic pile would have a similar effect provided the electric condition of its poles was more intense than that of the substances submitted to its action.

But, though this hypothesis applies to chemical changes very satisfactorily, and coincides with the laws of affinity, it would nevertheless be premature, as Sir H. Davy himself admits, to place entire confidence in it. For there is no proof that chemical attraction is owing to the cause supposed ; nor is it established with certainty that bodies do possess natural electric energies. It does not follow because they exhibit signs of electric excitement after contact, that they naturally possess one kind of electricity rather than another. As well might it be argued that a common stick of sealing wax is naturally negative, because it is excited negatively by friction, a mode of reasoning which is in opposition to the facts exhibited by electrical action. Another circumstance which seems unfavourable to the hypothesis, is the well-known fact, that one and the same substance is positive to some bodies and negative to others.

Whatever may be the fate of the electro-chemical hypothesis, it has conducted Sir H. Davy to one of the most brilliant discoveries ever made in chemistry. Regarding all compounds as constituted of oppositely electrical elements, he conceived that none of them could resist decomposition, if they were exposed to a battery of sufficient intensity ; and he accordingly subjected substances to its action, which till then had been regarded as simple, expecting that if they were compounds, they would be resolved into their elements. The result exceeded his expectations. The alkalis and earths were decomposed ; a substance with the aspect and properties of a metal appeared at the negative pole, while oxygen was disengaged at the positive surface. (Phil. Trans. for 1808.)

The same views have been applied successfully on a very recent occasion. It has been long known that the copper sheathing of vessels oxidizes very readily in sea water, and consequently wastes with such rapidity as to require frequent renewal. Sir H. Davy observed that the copper derived its oxygen from atmospheric air dissolved in the water, and that the oxide of copper then took muriatic acid from the soda and magnesia, forming with it a submuriate of the oxide of copper. Now, if the copper did not oxidize, it could not combine with muriatic acid ; and, according to Sir H. Davy, it only combines with oxygen, a negative electric, because it is in a state of positive electricity, which is natural to it. If therefore the copper could by any means be rendered negative, then the copper and the oxygen, being both in the same electrical condition, would have no tendency to unite. The object then was to render copper permanently negative. Now this is done by bringing copper in contact with zinc or iron ; for the former then becomes negative, and the latter positive.

Acting on this idea, it was found that the oxidation of the copper might be completely prevented. A piece of zinc as large as a pea, or the head of a small round nail, was found fully adequate to preserve forty or fifty square inches of copper ; and this wherever it was placed,

whether at the top, bottom, or middle of the sheet of copper, or under whatever form it was used. And when the connexion between different pieces of copper was completed by wires, or thin filaments of the 40th or 50th of an inch in diameter, the effect was the same; every side, every surface, every particle of the copper remained bright, whilst the iron or the zinc was slowly corroded. Sheets of copper defended by 1-40th to 1-1000th part of their surface of zinc, malleable and cast-iron, were exposed during many weeks to the flow of the tide in Portsmouth harbour, and their weight ascertained before and after the experiment. When the metallic protector was from 1-40th to 1-150th there was no corrosion nor decay of the copper; with smaller quantities, such as 1-200th to 1-460th, the copper underwent a loss of weight which was greater in proportion as the protector was smaller; and as a proof of the universality of the principle, it was found that even 1-1000th part of cast-iron saved a certain proportion of the copper. (Phil. Trans. for 1824.)

It is remarkable that the copper must not be rendered too strongly negative, otherwise the positive electric bodies, such as magnesia and lime, separate from the water during these electro-chemical changes, adhere to the copper, and form a nidus for sea-weeds and shell-fish. This happens when there is 1-35th to 1-80th of the protecting metal. With 1-150th no such deposits were noticed. From some further observations made by Sir H. Davy in the Phil. Trans. for 1825, there remains no doubt that the protecting process may be applied to ships on actual service with great advantage.

These principles may be usefully applied on other occasions. One obvious application of the kind, suggested by Mr Pepys, is to preserve iron or steel instruments from rust by contact with a piece of zinc. The iron or steel is thereby rendered negative, while the zinc, being positive, oxidizes with increased rapidity.

The best arrangement for exhibiting the chemical agency of galvanism is a battery composed of an extensive series of small plates. No advantage is derived from using plates of a large size, since the decomposing power of the Voltaic apparatus is dependent on the number of the plates rather than on their dimensions. The enormous battery of Mr Children decomposed water very slowly. An acid solution should be employed for exciting the battery, and its strength should be such as to cause a moderate, long-continued action, in preference to a violent and temporary one. Any of the stronger acids, as the nitric, sulphuric and muriatic, may be used for the purpose; but the last produces the most permanent effect, and is therefore preferable. The proportion should be one part of acid to 16 or 20 of water; or if the series is extensive, the acid may be still farther diluted with advantage.

III. The conditions necessary for igniting metallic wires or charcoal by the battery are different from those which have been recommended for procuring its other effects. Their ignition seems to arise from the electricity passing along them with difficulty; which, as they are perfect conductors, can take place only when the quantity to be transmitted is out of proportion to the extent of surface along which it has to pass. It is therefore an object to excite as large a quantity of electricity in a given time as possible, and for this purpose a very few large plates answer better than a great many small ones.

A strong acid solution may also be used; for an energetic action, though of short duration, is more important than a moderate one of

greater permanence. With this intention nitric acid may be employed with advantage.

IV. The power of lightning in destroying and reversing the polarity of a magnet, and of communicating magnetic properties to pieces of iron which did not previously possess them, has been known for some years, and had led to the supposition that similar effects might be produced by the common electrical or galvanic apparatus. Attempts were accordingly made to communicate the magnetic virtue by means of electricity or galvanism; but no results of importance were obtained till the winter of 1819, when Professor Oersted of Copenhagen made his famous discovery, which forms the basis of a new branch of science called electro-magnetism.

The fact observed by Professor Oersted was, that an electrical current, such as is supposed to pass from the positive to the negative pole of a Voltaic battery along a wire which connects them, causes a magnetic needle placed near it to deviate from its natural position, and assume a new one, the direction of which depends upon the mode of conducting the experiment. On placing the wire above the magnet and parallel to it, the pole next the negative end of the battery always moves westward, and when the wire is placed under the needle, the same pole goes towards the east. If the wire is on the same horizontal plane with the needle, no declination whatever takes place; but the magnet shows a disposition to move in a vertical direction, the pole next the negative side of the battery being depressed when the wire is to the west of it, and elevated when it is placed on the east side.

The extent of the declination occasioned by a battery depends upon its power, and the distance of the connecting wire from the needle. If the apparatus is powerful, and the distance small, the declination will amount to an angle of  $45^\circ$ . But this deviation does not give an exact idea of the real effect which may be produced by galvanism; for the motion of the magnetic needle is counteracted by the magnetism of the earth. When the influence of this power is destroyed by means of another magnet, the needle will place itself directly across the connecting wire; so that the real tendency of a magnet is to stand at right angles to an electric current.

The communicating wire is also capable of attracting and repelling the poles of a magnet. If, when the magnet and connecting wire are at right angles to each other, the latter passing across the centre of the former, the wire be moved along the needle towards either extremity, attraction will take place between the wire and the adjacent pole: and this will occur though the same point of the wire should be presented in succession to both of the poles. Again, if the position of the poles of the needle be reversed, they will be repelled by the same point of the wire which had previously attracted them\*.

This discovery was no sooner announced, than the experiments were repeated and varied by philosophers in all parts of Europe, and, as was to be expected, new facts were speedily brought to light. Among the most successful labourers in this field, M. M. Ampère, Arago, and Biot of Paris, and Sir H. Davy and Mr Faraday in this country, deserve to be particularly mentioned.

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\* The clearest statement of this fact which I have seen is in the historical sketch of Electro-magnetism by Mr Faraday. (*Annals of Philosophy. New Series, vol. ii.*)

M. Ampère observed that the Voltaic apparatus itself acted on a magnetic needle placed upon or near it in the same manner as the wire which united its two extremities. But the declination was found to occur only when the opposite ends of the battery were in communication, and ceased entirely as soon as the circuit was interrupted,—a difference which was supposed to arise from the passage of an uninterrupted electric current through the apparatus, as along the connecting wire, taking place in the first case, and not in the second. M. Ampère therefore proposed the magnetic needle as an instrument for discovering the existence and direction of an electric current, (or currents according to the theory of the two electricities) as well as for pointing out the proper state and fitness of a galvanic apparatus for electro-magnetic experiments in general.

M. Ampère soon after discovered that a power of attraction and repulsion might be communicated by an electric current alone, without the use of a magnet. Two wires of copper, brass, or any other metal, placed parallel to one another, and suspended so as to move freely, were connected with the opposite poles of a galvanic apparatus. If the electric current passed along both wires in the same direction, they attracted one another: if in an opposite direction, they repelled each other. The result of this experiment gave rise to the supposition that the magnetic property was actually communicated to the wires by the electric current; and this supposition was confirmed by M. Arago, who found that iron filings were attracted by a wire placed in the Voltaic circuit, and that they all fell off when the communication between the poles was interrupted. This fact was also discovered about the same time by Sir H. Davy, who has minutely described his experiments in a paper in the *Philosophical Transactions* for 1821.

The communication of temporary magnetic properties to the common metals naturally led to an attempt to magnetize steel and iron permanently by the same agent. The experiment was made by M. Arago and Sir H. Davy about the same time, and both of them were successful. Sir H. Davy attached steel needles to the connecting wire, some parallel to it, and others transversely. The former merely acted as a part of the circuit; they did not possess poles, and lost their power of attracting iron filings as soon as the electric current ceased to circulate through them. But the latter acquired a north and south pole, and preserved the property after separation from the wire. M. Arago at first operated in a similar manner; but, at the suggestion of M. Ampère, he made the connecting wire in the form of a spiral or helix, and placed the needle to be magnetized in the centre of it. By this arrangement the maximum effect was obtained in a shorter time than by any other method. Sir H. Davy also rendered a needle magnetic by placing it across a wire, along which a charge from a common Leyden battery was transmitted. This series of experiments was completed by M. Ampère's discovery, that a connecting wire, suspended so as to have perfect freedom of motion, was influenced by the magnetic attraction of the earth.

For the next fact of importance, science is indebted to the researches of Mr Faraday. He ascertained that the action of the connecting wire on the direction of a magnet, was not owing to any attraction or repulsion exerted between them, but to a tendency they have to revolve round each other. He contrived an apparatus, (*Quarterly Journal*, vol. xii.) by means of which either pole of a magnet was made to revolve round the wire as a fixed point; and then, by

fixing the wire, and giving free motion to the magnet, both poles of the latter were made to revolve in succession round the former.

He was also successful in causing the wire to revolve by the influence of the magnetism of the earth.

These magnetic properties of the Voltaic apparatus, which form the basis of the new science called electro-magnetism, were discovered soon after the original experiments of Oersted were made known to the public. Other facts of interest have since been observed, and some ingenious general views have been proposed to account for all the phenomena; but as a full discussion of electro-magnetism would lead into details too minute for an elementary treatise, I must refer the reader, who may wish for more ample information, to works written professedly on the subject. In addition to the papers already alluded to, the "*Recueil d'Observations Electro-dynamiques*" by M. Ampère, and the second edition of M. Barlow's *Essay on Magnetic Attractions*, will be consulted with much advantage.

### *On the Theory of the Pile.*

There are three theories concerning the action of the Voltaic pile or battery. The first originated with Volta, who conceived that the electricity was set in motion, and the supply kept up, solely by the contact of the metals. He regarded the interposed solutions merely as conductors, by means of which the electricity, developed by each pair of plates, was conveyed from one part of the apparatus to the other.

Volta, in forming his theory, left out of view the chemical changes going on between the metals and the fluids in contact with them; whereas it was apparent that these changes constituted an important, if not an essential, part of the process. For it was observed that no sensible effects were produced by a combination formed of substances which have no chemical action on each other; that the action of the pile is always accompanied by the oxidation of the zinc; and that its energy is almost in exact proportion to the rapidity with which the oxidation takes place. These observations induced Dr Wollaston to conclude that the process begins with the oxidation of the zinc—that the oxidation is the primary cause of the electric phenomena; and he published several ingenious experiments in the *Philosophical Transactions* for 1801 in support of his opinion. This forms the second theory of the pile, and is in direct opposition to that of Volta.

The third theory is intermediate between the two others, and was proposed by Sir H. Davy. He inferred from numerous experiments, that there is no reason to question the fact, originally stated by Volta, that the electric equilibrium is disturbed by the contact of different substances without any chemical action taking place between them; and his conclusions appear to be justified by subsequent observers. But he perceived, at the same time, that the chemical changes, though not the primary cause of the phenomena, are an essential part of the process; that without them no considerable degree of galvanic excitement can ever be produced. In his opinion, therefore, the action is commenced by the contact of the metals, and kept up by the chemical phenomena.

The mode in which Sir H. Davy conceives the chemical changes act, is by restoring the electric equilibrium whenever it is disturbed. By the contact of the zinc and copper plates, the former is rendered



positive throughout the whole series, and the latter negative; and by means of the conducting fluid with which the cells are filled, the positive electricity accumulates on one side of the battery, and the negative electricity on the other. But the quantity of electricity, thus excited, would not be sufficient, as is maintained, for causing an energetic action. For this effect, the electric equilibrium of each pair of plates must be restored as soon as it is disturbed, in order that they should be able to furnish an additional supply of electricity. The chemical substances of the solution are supposed to effect that object in the following manner. The negative ingredients of the liquid, such as oxygen and the acids, pass over to the zinc; while the hydrogen and the alkalies, which are positive, go to the copper; in consequence of which, both the metals are for the moment restored to their natural condition. But as the contact between them continues, the equilibrium is no sooner restored than it is again disturbed; and when, by a continuance of the chemical changes, the zinc and copper recover their natural state, electricity is again developed by a continuance of the same condition by which it was excited in the first instance. In this way Sir H. Davy explains why chemical action, though not essential to the first development of electricity, is necessary for enabling the Voltaic apparatus to act with energy.

## PART II.

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### *PRELIMINARY REMARKS.*

**I**N teaching a science, the details of which are numerous and complicated, it would be injudicious to follow the order of discovery and proceed from the individual facts to the conclusions which have been deduced from them. An opposite course is indispensable. It is necessary to discuss the general principles in the first instance, in order to aid the beginner in remembering the insulated facts, and comprehending the explanations connected with them.

This necessity is in no case more sensibly felt than in the study of chemistry, and for this reason I shall commence the second part of the work by explaining the leading doctrines of the science. One inconvenience, indeed, does certainly arise from this method. It is often necessary, by way of illustration, to refer to facts of which the beginner is ignorant; and therefore on some occasions more knowledge will be required for understanding a subject fully, than the reader may have at his command. But these instances will, it is hoped, be rarely met with; and when they do occur, the reader is advised to quit the point of difficulty, and return to the study of it, when he shall have acquired more extensive knowledge of the details.

To the chemical history of each substance its chief physical characters will be added. A knowledge of these properties is not only advantageous in assisting the chemist to distinguish one body from another, but in many instances is put to uses still more important. The specific gravity in particular is of great consequence; and as this expression will hereafter be used in almost every page, it will be proper, before proceeding farther, to explain the meaning of it. Equal bulks of different substances, as a cubic inch of gold, silver, tin and water, differ more or less in weight: their densities are different; or, in other words, they contain different quantities of ponderable matter in the same space. The tin will weigh eight times more than the water, the silver about ten times and a half, and the gold upwards of 19 times more than that fluid. The density of all solids and liquids may be determined in the same manner; and if they are compared with an equal bulk of water as a standard of comparison, a series of numbers will be obtained, which will show the comparative density or specific gravity, as it is called, of all of them.

The process for determining specific gravities is therefore sufficiently simple. It consists in weighing a body carefully, and then determining the weight of an equal bulk of water, the latter being regarded as unity. If, for example, a portion of water weighs nine grains, and the same bulk of another body 20 grains, its density is de-

terminated by the formula, as  $9 : 20 :: 1$  (the specific gravity of water) to the fourth proportional 2.2222; so that the specific gravity of any substance is found by dividing its weight by the weight of an equal volume of water. It is easy to discover the weight of equal bulks of water and any other liquid by filling a small bottle of known weight with each successively, and weighing them\*. The method of obtaining the necessary data in case of a solid is somewhat different. The body is first weighed in air, is next suspended in water by means of a hair attached to the scale of the balance, and is then weighed again. The difference gives the weight of a quantity of water equal to the bulk of the solid. Or the bottle recommended for taking the specific gravity of liquids may be employed. After weighing the bottle filled with water, a known weight of the solid is put into it, which of course displaces a quantity of water precisely equal to its own volume. The exact weight of the displaced water is found by weighing the bottle again, after having wiped the outside of it with a dry cloth.

The determination of the specific gravity of gaseous substances is an operation of much greater delicacy. From the extreme lightness of gases, it would be inconvenient to compare them with an equal bulk of water, and therefore atmospheric air is taken as the standard of comparison. The first step of the process is to ascertain the weight of a given volume of air. This is done by weighing a very light glass flask, furnished with a good stopcock, while full of air; and then weighing it a second time, after the air has been withdrawn by means of the air-pump. The difference between the two weights gives the information required. According to the experiments of Sir George Shuckburgh, 100 cubic inches of pure and dry atmospheric air, at the temperature of  $60^{\circ}$  F. and when the barometer stands at 30 inches, weigh precisely 30.5 grains. By a similar method the weight of any other gas may be determined, and its specific gravity be inferred accordingly. Thus, suppose 100 cubic inches of oxygen are found to weigh 33.888 grains, its specific gravity will be thus deduced; as  $30.5 : 33.888 :: 1$  (the sp. gr. of air) : 1.1111 the sp. gr. of oxygen.

There are four circumstances to which particular attention must be paid in taking the specific gravity of gases.

1. The gas should be perfectly pure, otherwise the result cannot be accurate.
2. Due regard must be had to its hygrometric condition. If it is saturated with moisture, the necessary correction may be made for that circumstance by the formula page 51; or it may be dried by the use of substances, which have a powerful attraction for moisture, such as the chloride of calcium, quicklime, or fused potash.
3. As the bulk of gaseous substances, owing to their elasticity and compressibility, is dependent on the pressure to which they are exposed, no two observations would admit of comparison, unless they were made under the same elevation of the barometer. It is always understood, in taking the specific gravity of a gas, that the barometer must stand at 30 inches, by which means the operator is certain that each gas is subject to equal degrees of compression. An elevation of 30 inches is therefore called the standard height; and if the mercurial

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\* Bottles are prepared for this purpose by the Philosophical Instrument-makers.

column be not of that length at the time of performing the experiment, the error arising from this cause must be corrected by calculation. It has been established by careful experiments that the bulk of gases is inversely as the pressure. Thus, 100 measures of air under the pressure of a thirty inch column of mercury, will dilate to 200 measures, if the pressure be diminished by one half; and will be compressed to 50 measures, when the pressure is equal to a mercurial column of 60 inches. The correction for the effect of pressure may therefore be made by the rule of three, as will appear by an example. If a certain portion of gas occupy the space of 100 measures at 29 inches of the barometer, its bulk at 30 inches may be obtained by the following proportion; as

$$30 : 29 :: 100 : 96.66.$$

4. For a similar reason the temperature should always be the same. The standard or mean temperature is 60° F.; and if the gas be admitted into the weighing flask when the thermometer is above or below that point, the formula of page 29 should be employed for making the necessary correction.

Chemistry is indebted for its nomenclature to the labours of four celebrated chemists, Lavoisier Berthollet, Guyton-Morveau, and Fourcroy. The principles which guided them in its construction are exceedingly simple and ingenious. The known elementary substances and the more familiar compound ones were allowed to retain the appellations which general usage had assigned to them. The newly discovered elements were named from some striking property. Thus, as it was supposed that acidity was always owing to the presence of the vital air discovered by Priestley and Scheele, they give it the name of oxygen, derived from two Greek words signifying generator of acid; and they called inflammable air hydrogen, from the circumstances of its entering into the composition of water.

Compounds of which oxygen forms a part were called acids or oxides according as they do or do not possess acidity. An oxide of iron or copper signifies a combination of those metals with oxygen, which has no acid properties. The name of an acid was derived from the substance acidified by the oxygen, to which was added the termination in *ic*. Thus, sulphuric and carbonic acids signify acid compounds of sulphur and carbon with oxygen gas. If sulphur or any other body should form two acids, that which contains the least quantity of oxygen is made to terminate in *ous*, as sulphurous acid. The termination in *uret* was intended to denote combinations of the simple non-metallic substances either with one another, with a metal, or with a metallic oxide. Sulphuret and carburet of iron, for example, signify compounds of sulphur and carbon with iron. The different oxides or sulphurets of the same substance were distinguished from one another, by some epithet, which was commonly derived from the colour of the compound, such as the black and red oxides of iron, the black and red sulphurets of mercury. Though this practice is still continued occasionally, it is now more customary to distinguish degrees of oxidation by the use of derivatives from the Greek. Protoxide signifies the first degree of oxidation, deutoxide the second, tritoxide the third, and peroxide the highest. The sulphurets, carburets, &c. of the same substance are designated in a similar way. The combination of acids with alkalies, earths, or metallic oxides, were termed salts, the names

of which were so contrived as to indicate the substances contained in them. If the acidified substance contains a maximum of oxygen, the name of the salt terminates in *ate*; if a minimum, the termination in *ite* is employed. Thus, the sulphate, phosphate, and arseniate of potash, are salts of sulphuric, phosphoric, and arsenic acids; while the terms sulphite, phosphite, and arsenite of potash, denote combinations of that alkali with the sulphurous, phosphorous, and arsenious acids.

The advantage of a nomenclature which disposes the different parts of a science in so systematic an order, and gives such powerful assistance to the memory, is incalculable. The principle has been acknowledged in all countries where chemical science is cultivated, and the minutest details of it have been adopted in Britain. It must be admitted, indeed, that some parts of it are defective. The erroneous idea of oxygen being the general acidifying principle, has exercised an injurious influence over the whole structure. It would have been convenient also to have had a different name for hydrogen. But it is now too late to attempt a change; for the confusion attending such an innovation would more than counterbalance its advantages. The original nomenclature has therefore been preserved, and such additions made to it as the progress of the science rendered necessary. The most essential improvement has been suggested by the discovery of the laws of chemical combination. The different salts formed of the same constituents were formerly divided into *neutral*, *super*, and *sub*-salts. They were called neutral if the acid and alkali are in the proportion for neutralizing one another; super-salts, if the acid prevails; and sub-salts, if the alkali is in excess. The name is now regulated by the atomic constitution of the salt. If it be a compound of one atom of the acid to one atom of the alkali, the generic name of the salt is employed without any other addition; but if two or more atoms of the acid be attached to one of the base, or two or more atoms of the base to one of the acid, a numeral is prefixed so as to indicate its composition. The two salts of sulphuric acid and potash are called sulphate and *bi*-sulphate; the first containing one atom of the acid to one atom of the alkali, and the latter, two of the former to one of the latter. The three salts of oxalic acid and potash are termed the oxalate, *bin*oxalate, and *quad*roxalate of potash; because one atom of the alkali is united with one atom of acid in the first, with two in the second, and with four in the third salt. As the numerals which denote the atoms of the acid in a super-salt are derived from the Latin language, Dr Thomson proposes to employ the Greek numerals, *dis*, *tris*, *tetrakis*, to signify the atoms of alkali in a sub-salt.

This method is in the true spirit of the original framers of our nomenclature. Chemists have already begun to apply the same principle to other compounds besides salts; and there can be no doubt that it will be applied universally whenever our knowledge shall be in a state to admit of it.



## SECTION I.

*AFFINITY.*

All chemical phenomena are owing to Affinity or chemical attraction. It is the basis on which the science of chemistry is founded. It is, as it were, the instrument which the chemist employs in all his operations, and hence forms the first and leading object of his study.

Affinity is exerted between the minutest particles of different kinds of matter, causing them to combine so as to form new bodies endowed with new properties. It acts only at insensible distances; in other words, apparent contact, or the closest proximity, is necessary to its action. Every thing which prevents such contiguity is an obstacle to combination, and any force which increases the distance between particles already combined, tends to separate them permanently from each other. In the first case, they do not come within the sphere of their mutual attraction; in the second, they are removed out of it. It follows, therefore, that though affinity is regarded as a specific power distinct from the other forces which act on matter, its action may be promoted, modified or counteracted by several circumstances; and consequently, in studying the phenomena produced by affinity, it is necessary to begin by inquiring into the conditions that influence its operation.

The most simple instance of the exercise of chemical attraction is afforded by the mixture of two substances with one another. Water and sulphuric acid, or water and alcohol, combine readily. On the contrary, water shows little disposition to unite with sulphuric ether, and still less with oil; for however intimately their particles may be mixed together, they are no sooner left at rest than the ether separates almost entirely from the water, and a total separation takes place between that fluid and the oil. Sugar dissolves very sparingly in alcohol, but to any extent in water; while camphor is dissolved in very small quantity by water, and abundantly by alcohol. It appears, from these examples, that chemical attraction is exerted between different bodies with different degrees of force. There is sometimes no proof of its existence at all; between some substances it acts very feebly, and between others with great energy.

Simple combination of two principles is a common occurrence. The solution of salts in water, the combustion of phosphorus in oxygen gas, and the neutralization of a pure alkali by an acid, are instances of the kind. The phenomena however are often more complex. It frequently happens that the formation of a new compound is attended by the destruction of an existing one. The only condition necessary for this effect is the presence of some third body which has a greater affinity for one of the elements of a compound than they have for one another. Thus, oil has an affinity for the volatile alkali, ammonia, and will unite with it, forming a soapy substance called a liniment. But the ammonia has a still greater attraction for sulphuric acid; and hence if the acid be added to the liniment, the alkali will quit the oil, and unite by preference with the acid. If a solution of camphor in alcohol be poured into water, the camphor will be set free, because the alcohol combines with the water. Sulphuric acid, in like manner, separates baryta from muriatic acid. Combination and de-

composition occur in each of these cases ;—combination of the sulphuric acid with the ammonia, of the water with the alcohol, and of the baryta with the sulphuric acid ;—decomposition of the compounds formed of the oil and ammonia, of the alcohol and camphor, and of the muriatic acid and baryta. These are examples of what Bergmann called single elective affinity ;—elective, because a substance manifests, as it were, a choice for one of two others, uniting with it by preference, and to the exclusion of the other. Many of the decompositions that occur in chemistry are instances of single elective affinity.

The order in which these decompositions take place has been expressed in tables ; of which the following, drawn up by Geoffroy, is an example :—

*Sulphuric Acid.*

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Baryta,  
Strontia,  
Potash,  
Soda,  
Lime,  
Ammonia,  
Magnesia.

This table signifies, first, that sulphuric acid has an affinity for the substances placed below the horizontal line, and can therefore unite separately with each of them ; and, secondly, that the base of the salts so formed will be separated from the acid by adding any of the alkalies or earths which stand above it in the column. Thus ammonia will separate magnesia, lime ammonia, and potash lime ; but none of them can withdraw baryta from sulphuric acid, nor can ammonia or magnesia decompose the sulphate of lime, though strontia or baryta will do it. Bergmann conceived that these decompositions were solely determined by chemical attraction, and that consequently the order of decomposition represented the comparative forces of affinity ; and this view, from the simple and natural explanation it afforded of the phenomenon, was for a time very generally adopted. But Bergmann was in error. It does not necessarily follow, because lime can separate ammonia from sulphuric acid, that the lime has a greater attraction for the acid than the volatile alkali. Other causes are in operation which modify the action of affinity to such a degree, that it is impossible to discover how much of the effect is owing to that power. It is conceivable that the ammonia may in reality have a stronger attraction for sulphuric acid than lime, and yet the lime, from the great influence of disturbing causes, might succeed in decomposing the sulphate of ammonia.

The justice of the foregoing remark will be made obvious by the following example :—When a stream of hydrogen gas is passed over the oxide of iron heated to redness, it deprives the iron of its oxygen entirely, combining with it so as to form water. On the contrary, when watery vapour is brought into contact with red-hot metallic iron, the oxygen of the water quits the hydrogen and combines with the iron. It follows from the result of the first experiment, according to Bergmann, that hydrogen has a stronger attraction for oxygen than iron ; and from that of the second, that iron has a greater affinity for oxygen than hydrogen. But these inferences are incompatible with one ano-

ther. The affinity of hydrogen for oxygen must either be equal to that of iron, or greater or less. If the first is the case, then the result of both experiments was determined by modifying circumstances; since neither of these substances ought on this supposition to take oxygen from the other. If the second, then the decomposition in one of the experiments must have been determined by extraneous causes in direct opposition to the tendency of affinity.

To Berthollet is due the honour of pointing out the fallacy of Bergmann's opinion. He was the first to show that the relative forces of chemical attraction cannot always be determined by observing the order in which substances separate each other when in combination, and that the tables of Geoffroy are merely tables of decomposition, not of affinity. He likewise traced all the various circumstances that modify the action of affinity, and gave a consistent explanation of the mode in which they operate. Berthollet went even a step farther. He denied the existence of elective affinity as an invariable force, capable of effecting the perfect separation of one body from another; he maintained that all the instances of complete decomposition attributed to elective affinity are in reality determined by one or more of the collateral circumstances that influence its operation. But here this acute philosopher has surely gone too far. Bergmann is admitted to have erred in supposing that the result of chemical action is in every case owing to elective affinity; but Berthollet certainly ran into the opposite extreme in declaring that the effects formerly ascribed to that power are never produced by it. That chemical attraction is exerted between bodies with different degrees of energy is indisputable. Water has a much greater affinity for muriatic acid and ammoniacal gases than for carbonic acid and sulphuretted hydrogen, and for these than for oxygen and hydrogen. The attraction of lead for oxygen is greater than that of silver for the same substance. The disposition of gold and silver to combine with mercury, is greater than the attraction of platinum and iron for that fluid. As these differences cannot be accounted for by the operation of any modifying causes, we must admit a difference in the force of affinity in producing combination. It is equally clear that in some instances the separation of bodies from one another can only be explained on the same principle. No one, I conceive, will contend that the decomposition of hydriodic acid by chlorine, or of sulphuretted hydrogen by iodine, is determined by the concurrence of any modifying circumstances.

Affinity is the cause of still more complicated changes than those which have been just considered. In a case of single elective affinity three substances only are present, and two affinities are in play. But it frequently happens that two compounds are mixed together, and four different affinities brought into action. The changes that may or do occur under these circumstances are most conveniently studied by aid of a diagram,—a method which was first employed, I believe, by Dr Black, and has since been generally practised. Thus, in mixing together a solution of the carbonate of ammonia and muriate of lime, their mutual action may be represented in the following manner:



Each of the acids has an attraction for both the bases, and hence it is possible either that the two salts should continue as they are, or that an interchange of principles should ensue, giving rise to two new compounds,—the carbonate of lime and muriate of ammonia. According to the views of Bergmann the result is solely dependent on the comparative strength of affinities. If the affinity of the carbonic acid for the ammonia, and of the muriatic acid for the lime, exceed that of the carbonic acid for lime, added to that of the muriatic acid for ammonia, then will the two salts experience no change whatever; but if the latter affinities preponderate, then, as does actually happen in the present example, both the original salts will be decomposed, and two new ones generated. Two decompositions and two combinations take place, being an instance of what is called double elective affinity. Mr Kirwan applied the terms quiescent and divellent to denote the tendency of the opposing affinities, the action of the former being to prevent a change, the latter to produce it.

The doctrine of double elective affinity was assailed by Berthollet on the same ground and with the same success as in the case of single elective attraction. He succeeded in proving that the effect cannot always be ascribed to the sole influence of affinity. For, to take the example already adduced, if the carbonate of ammonia decompose the muriate of lime by the mere force of a superior attraction, it is manifest that the carbonate of lime ought never to decompose the muriate of ammonia. But if these two salts are mixed in a dry state and exposed to heat, double decomposition does take place, carbonate of ammonia and muriate of lime being formed; and therefore if the change in the first example was produced by chemical attraction alone, that in the second must have occurred in direct opposition to that power. It does not follow, however, because the result is sometimes determined by modifying conditions, that it must always be so. I apprehend that the decomposition of the solid cyanuret of mercury by sulphuretted hydrogen gas, which takes place even at a low temperature, cannot be ascribed to any other cause than a preponderance of the divellent over the quiescent affinities.

## On the Changes that accompany Chemical Action.

The leading circumstance that characterises chemical action is the loss of properties experienced by the combining substances, and the acquisition of new ones by the product of their combination. The change of property is sometimes inconsiderable. In a solution of sugar or salt in water, and in mixtures of water with alcohol or sulphuric acid, the compound retains so much of the character of its constituents, that there is no difficulty in recognising their presence. But more generally the properties of one or both of the combining bodies disappear entirely. No ingenuity could guess *a priori*, that water is a compound body, much less that it is composed of two gases, oxygen and hydrogen, neither of which, when uncombined, has ever been compressed into a liquid. Hydrogen is one of the most inflammable substances in nature, and yet water cannot be set on fire; oxygen, on the contrary, enables bodies to burn with great brilliancy, and yet water extinguishes combustion. The alkalis and earths were regarded as simple till Sir H. Davy proved them to be compounds, and certainly they evince no sign whatever of containing oxygen gas and a metal. Numerous examples of a similar kind are afforded by the action of acids and alkalis on one another. Sulphuric acid and potash, for example, are highly caustic. The former is intensely sour, reddens the blue colour of vegetables, and has a strong affinity for alkaline substances; the latter has a pungent taste, converts the blue colour of vegetables to green, and combines readily with acids. On adding these principles cautiously to one another, a compound results called a neutral salt, which does not in any way affect the colouring matter of plants, and in which the other distinguishing features of the acid and alkali can no longer be perceived. They appear to have destroyed the properties of each other, and are hence said to neutralize one another.

The other phenomena that accompany chemical action are changes of density, temperature, form and colour.

It is observed that two bodies rarely occupy the same space after combination which they did separately. In general their bulk is diminished, so that the specific gravity of the new body is greater than the mean of its components. Thus, a mixture of 100 equal measures of water and an equal quantity of sulphuric acid do not occupy the space of 200 measures, but considerably less. A similar contraction frequently attends the combination of solids. Gases often experience a remarkable condensation when they unite. The elements of olefiant gas, for instance, would expand to four times the bulk of that compound, if they were suddenly to become free, and assume the gaseous form. But the rule is not without exception. The reverse happens in some metallic compounds; and there are examples of combination between gases without any change of bulk.

2. A change of temperature generally accompanies chemical action. Caloric is evolved either when there is a diminution in the bulk of the combining substances without a change of form, or when a gas is condensed into a liquid, or when a liquid becomes solid. The heat caused by mixing sulphuric acid with water is an instance of the former; and the common process of slaking lime, during which water loses its liquid form, in combining with that earth, is an example of the second. The rise of temperature in these cases is obviously referable to a diminution in the capacity of the new compound for caloric; but an in-



tense degree of heat sometimes accompanies chemical action under circumstances in which an explanation founded on a change of specific caloric is quite inadmissible. At present it is enough to have stated the fact; the theory of it will be discussed under the subject of combustion. The production of cold seldom or never takes place during combination, except when the specific caloric is suddenly increased by the conversion of a solid into a liquid, or a liquid into a gas. All the frigorific mixtures act in this way.

3. The changes of form that attend chemical action are exceedingly various. The combination of gases may give rise to a liquid or a solid; solids sometimes become liquid, or liquids solid. Several familiar chemical phenomena, such as explosions, effervescence, and precipitations, are owing to these changes. The sudden evolution of a large quantity of gaseous matter occasions an explosion, as when gunpowder detonates. The slower disengagement of a gas causes effervescence, as occurs when marble is put into muriatic acid. A precipitate is owing to the formation of a new body which happens to be insoluble in the liquid in which its elements were dissolved.

4. The colour of a compound is frequently quite different from that of the substances which form it. There does not appear to be any uniform relation between the colour of a body and that of its elements, so that it is not possible to anticipate the colour of any particular compound by knowing the principles which enter into its composition. Iodine, whose vapour is of a violet hue, forms a beautiful red compound with mercury, and a yellow one with lead. The brown oxide of copper generally gives rise to green and blue coloured salts; while the salts of the oxide of lead, which is itself yellow, are for the most part colourless. The colour of precipitates is a very important study, as it often enables the chemist to distinguish bodies from one another when in solution.

### *On the Circumstances that modify and influence the Operation of Affinity.*

Of the conditions which are capable of promoting or counteracting the tendency of chemical attraction, the following are the most important: cohesion, elasticity, quantity of matter, and gravity. To these may be added the agency of the imponderables.

#### *Cohesion.*

The first and obvious effect of cohesion is to oppose affinity, by impeding or preventing that mutual penetration and close proximity of the particles of different bodies, which is essential to the successful exercise of their attraction. For this reason bodies seldom act chemically in their solid state; their molecules do not come within the sphere of attraction, and therefore combination cannot take place, although their affinity may in fact be considerable. Liquidity, on the contrary, favours chemical action; it permits the closest possible approximation, while the cohesive power is comparatively so trifling as to oppose no appreciable barrier to affinity.

Cohesion may be diminished in two ways, either by mechanical division, or by the application of heat. The former is useful by increasing the extent of surface; but it is not of itself in general sufficient,

because the particles, however minute, still retain that degree of cohesion which constitutes solidity. Caloric acts with greater effect, and never fails in promoting combination, whenever the cohesive power is a barrier to it. Its intensity should always be so regulated as to produce liquefaction. It is often enough to liquefy one of the substances, as is proved by the facility with which water dissolves many salts and other solid bodies. But it is easy to perceive that the cohesive power is still in operation: for a solid is commonly dissolved in greater quantity when its cohesion is diminished by caloric. The reduction of both substances to the liquid state is the best method for ensuring chemical action. The slight degree of cohesion possessed by liquids does not appear to cause any impediment to combination; for they commonly act as energetically on each other at low temperatures, or at a temperature just sufficient to cause perfect liquefaction, as when their cohesive power is still further diminished by caloric. It seems fair to infer, therefore, that no affinity exists between two bodies which do not combine when they are intimately mixed in a liquid state.

The phenomena of crystallization are owing to the ascendancy of cohesion over affinity. When a large quantity of salt has been dissolved in water by the aid of heat, a portion of it separates as the solution cools, because the cohesive power of the salt then becomes comparatively too powerful for chemical attraction. Its particles begin to cohere together, and are deposited as crystals, the process of crystallization continuing till it is arrested by the affinity of the liquid. A similar change happens, when a solution made in the cold is gradually evaporated. The cohesion of the saline particles is no longer counteracted by the affinity of the liquid, and the salt therefore assumes the solid form.

Cohesion plays a still more important part. It sometimes determines the result of chemical action, probably even in opposition to affinity. Thus, on mixing together two acids and one alkali, of which two salts may be formed, one soluble, and the other insoluble, the alkali will unite with that acid, with which it forms the insoluble compound, to the total exclusion of the other. This is one of the modifying circumstances employed by Berthollet to account for the phenomena of single elective attraction, and it certainly is applicable to many of the instances to be found in the tables of affinity. When, for example, muriatic acid, sulphuric acid, and baryta, are mixed together, the sulphate of baryta is formed in consequence of its insolubility. Lime, which forms an insoluble salt with carbonic acid, separates that acid from ammonia, potash, and soda, with all of which it makes soluble compounds.

A similar explanation may be given of many cases of double elective attraction. If four substances, A, B, C, D, are mixed together in solution, of which it is possible to form four compounds, AB, CD, or AC, BD, that compound will certainly be produced, which happens to be insoluble. Thus, sulphuric acid, soda, muriatic acid, and baryta, may give rise either to sulphate of soda and muriate of baryta, or sulphate of baryta and muriate of soda; but the first two salts cannot exist together in the same liquid, because the insoluble sulphate of baryta is instantly generated, and its formation necessarily causes the muriatic acid to combine with the soda. In like manner, the muriate of lime is decomposed by the carbonate of ammonia, in consequence of the insolubility of the carbonate of lime.

*Elasticity.*

From the obstacle which cohesion puts in the way of affinity, the gaseous state, in which the cohesive power is wholly wanting, might be expected to be peculiarly favourable to chemical action. The reverse, however, is the fact. Bodies evince little disposition to unite when presented to each other in the elastic form. Combination does indeed sometimes take place, in consequence of a very energetic attraction; but examples of an opposite kind are much more common. Oxygen and hydrogen, and chlorine and hydrogen, though their mutual affinity is very powerful, may be preserved together for any length of time without combining. The cause of this is obviously the distance between the particles preventing that close approximation which is so necessary to the successful exercise of affinity. Hence many gases cannot be made to unite directly, which nevertheless combine readily while in their nascent state; that is, while in the act of assuming the gaseous form by the decomposition of some of their solid or fluid combinations.

Elasticity operates likewise as a decomposing agent. If two gases, whose reciprocal attraction is feeble, suffer considerable condensation when they unite, the compound will be decomposed by very slight causes. The chloride of nitrogen, which is an oily-like liquid, composed of the two gases chlorine and nitrogen, answers this description completely; and it is remarkable for being the most explosive substance hitherto discovered. A slight elevation of temperature, by increasing the natural elasticity of the two gases, or the contact of substances which have an affinity for either of them, produces an immediate explosion.

Many familiar phenomena of decomposition are owing to elasticity. All compounds that contain a volatile and a fixed principle, are liable to be decomposed by a high temperature. The expansion occasioned by caloric removes the elements of the compound to a greater distance from one another, and thus, by diminishing the force of chemical attraction, favours the tendency of the volatile principle to assume the form which is natural to it. The evaporation of water from a solution of salt is an instance of this kind.

Many solid substances which contain water in a state of intimate combination, part with it in a strong heat, in consequence of the volatile nature of that liquid. The separation of oxygen from some metals, by heat alone, is explicable on the same principle.

It appears from these, and some preceding remarks, that the influence of caloric over affinity is variable; for at one time it promotes chemical union, and opposes it at another. Its action, however, is always consistent. Whenever the cohesive power is an obstacle to combination, caloric favours affinity, as by diminishing the cohesion of a solid, or by converting a solid into a liquid. As the cause of the gaseous state, on the contrary, it keeps particles at a distance which would otherwise unite; or by producing expansion, it tends to separate substances from one another, which are already combined. There is one effect of caloric which seems somewhat anomalous; namely, the combination of gases on the approach of flame. The explanation given of it by Berthollet is probably correct,—that the sudden dilatation of the gases in the immediate vicinity of the flame, acts as a violent compressing power to the contiguous portions, and thus brings them within the sphere of their attraction.

Some of the decompositions, which were attributed by Bergmann to the sole influence of an elective affinity, may be ascribed to elasticity. If three substances are mixed together, two of which can form a compound which is less volatile than the third body, the last will, in general, be completely driven off by the application of heat. The decomposition of muriate of ammonia, or the salts of ammonia by lime, or any of the pure alkalies or alkaline earths, is an example of it; and for the same reason, all the carbonates are decomposed by muriatic acid, and all the muriates by sulphuric acid. This explanation applies equally well to some cases of double decomposition. It explains, for instance, why the dry carbonate of lime will decompose the muriate of ammonia by the aid of heat; for the carbonate of ammonia is more volatile than the muriate, either of ammonia or of lime.

### Quantity of Matter.

The influence of quantity of matter over affinity is universally admitted. If one body A unites with another body B in several proportions, that compound will be most difficult of decomposition, which contains the smallest quantity of B. Of the three oxides of lead, for instance, the peroxide parts most easily with its oxygen by the action of caloric; a higher temperature is required to decompose the deutoxide, and the protoxide will bear the strongest heat of our furnaces, without losing a particle of its oxygen.

The influence of quantity over chemical attraction may be further illustrated by the phenomena of solution. When equal weights of a soluble salt are added in succession to a given quantity of water which is capable of dissolving almost the whole of the salt employed, the first portion of the salt will disappear more readily than the second, the second than the third, the third than the fourth, and so on. The affinity of the water for the saline substance diminishes with each addition, till at last it is weakened to such a degree as to be unable to overcome the cohesion of the salt. The process then ceases, and a saturated solution is obtained.

Quantity of matter is employed advantageously in many chemical operations. If, for instance, a chemist is desirous of separating an acid from a metallic oxide by means of the superior affinity of potash for the former, he frequently uses rather more of the alkali than is sufficient for neutralizing the acid. He takes the precaution of employing an excess of alkali, in order the more effectually to bring every particle of the substance to be decomposed in contact with the decomposing agent.

But Berthollet has attributed a much greater influence to quantity of matter. It was the basis of his doctrine, developed in the *Statique Chimique*, that bodies cannot be wholly separated from each other by the affinity of a third substance for one element of a compound; and to explain why a superior chemical attraction does not produce the effect which might be expected from it, he contended that quantity of matter compensated for a weaker affinity. From the co-operation of several disturbing causes, Berthollet perceived that the force of affinity cannot be estimated with certainty by observing the order of decomposition; and he therefore had recourse to another method. He set out by supposing that the affinity of different acids for the same alkali is in the inverse ratio of the ponderable quantity of each

which is necessary for neutralizing equal quantities of the alkali. Thus, if two parts of one acid A, and one part of another acid B, are required to neutralize equal quantities of the alkali C, it was inferred that the affinity of B for C was twice as great as that of A. He conceived, further, that as two parts of A produce the same neutralizing effect as one part of B, the attraction exerted by any alkali towards the two parts of A ought to be precisely the same as for the one part of B; and he hence concluded that there is no reason why the alkali should prefer the small quantity of one to the large quantity of the other. On this he founded the principle that quantity of matter compensates for force of attraction.

Berthollet has here obviously confounded two things, namely, force of attraction and neutralizing power, which are really different, and ought to be held distinct. The relative weights of muriatic and sulphuric acids required to neutralize an equal quantity of any alkali, or, in other words, their capacities of saturation, are as 37 to 40, a ratio which remains constant with respect to all other alkalies. The affinity of these acids will, according to Berthollet's rule, be expressed by the same numbers. But in taking this estimate, we have to make three assumptions, all of which are disputable. There is no proof, in the first place, that muriatic acid has a greater affinity for an alkali, such as potash, than sulphuric acid. Such an inference would be directly opposed to the general opinion founded on the order of decomposition; and though that order is by no means a satisfactory test of the strength of affinity, it would be improper to adopt an opposite conclusion without having good reasons for doing so. Secondly, were it established that muriatic acid has the greatest affinity, it does not follow that the attraction of those acids for potash is in the ratio of 37 to 40. And, thirdly, supposing this point settled, it is very improbable that the ratio of their affinity for one alkali will apply to all others; analogy would lead us to anticipate the reverse. Independently of these objections, M. Dulong has found that the principle of Berthollet is not in accord with the results of experiment.

Though this mode of determining the relative forces of affinity cannot be admitted, it is possible that quantity of matter may some how or other compensate for a weaker affinity, and Berthollet attempts to prove it by experiment. On boiling the sulphate of baryta with an equal weight of pure potash, the alkali is found to have deprived the baryta of a small portion of its acid; and on treating oxalate of lime with nitric acid, some nitrate of lime is generated. As these partial decompositions are contrary to the supposed order of elective affinity, it was conceived that they were produced by quantity of matter acting in opposition to force of attraction. But they by no means justify such a conclusion. In the decomposition of sulphate of baryta by potash\*, no care was taken to exclude the atmospheric air during the operation: the alkali must consequently have absorbed carbonic acid; and it is an established fact that carbonate of potash decomposes partially the sulphate of baryta. A similar omission appears to have been made in the other experiments where decomposition was attempted by pure potash or soda. In many instances the result may fairly be attributed to other causes. Acids and alkalies have a tendency to unite in more than one proportion, and will readily form salts with excess of acid or of base when circumstances are favourable to their production.

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\* Researches into the Laws of Affinity.



This explains why nitrate of potash cannot be entirely decomposed by a quantity of sulphuric acid which is just sufficient for neutralizing the alkali. The sulphuric acid, instead of taking the whole of the potash, unites with a part of it, and forms the bisulphate. This tendency to the formation of an acid salt accounts for the fact quite satisfactorily; nor is there any reason to infer the co-operation of any other cause. Another circumstance that influences the result of such experiments, and which Berthollet left out of view entirely, is the affinity of salts for one another. On the whole, therefore, we may infer that Berthollet has given no satisfactory case in which quantity of matter is proved to compensate for a weaker affinity. Saline substances, indeed, seem ill adapted to such researches. For it is impossible in many, if not in most cases, to decide upon the relative strength of attraction of two acids for an alkali, or of two alkalies for an acid, which nevertheless is an important element in the inquiry; and even did we possess such knowledge, the influence of modifying circumstances is such, that it is difficult to appreciate the share they may have in producing a given effect.

### *Gravity.*

The influence of gravity is perceptible when it is wished to make two substances unite the densities of which are different. In a case of simple solution, a larger quantity of saline matter is found at the bottom than at the top of the liquid, unless the solution shall have been well mixed subsequently to its formation. In making an alloy of two metals which differ from one another in density, a larger quantity of the heavier metal will be found at the lower than in the upper part of the compound, unless great care be taken to counteract the tendency of gravity by agitation. This force obviously acts, like the cohesive power, in preventing a sufficient degree of approximation.

### *Imponderables.*

The influence which caloric exerts over chemical phenomena, and the modes in which it operates, have been already discussed. The chemical agency of galvanism has also been described. The effects of light will be most conveniently stated in other parts of the work. Electricity is frequently employed to produce the combination of gases with one another, and in some instances to separate them. It appears to act by the heat which it occasions, and therefore on the same principle as flame.

### *On the Measure of Affinity.*

As the foregoing observations prove that the order of decomposition is not always a satisfactory measure of affinity, it becomes a question whether there are any means of determining the comparative forces of chemical attraction. When no disturbing causes operate, the phenomena of decomposition afford a sure criterion; but when the conclusions obtained in this way are doubtful, assistance may be frequently derived from other sources. The surest indications are procured by observing the tendency of different substances to unite with the same principle, under the same circumstances, and subsequently by marking the comparative facility of decomposition when the compounds so formed are exposed to the same decomposing agent. Thus on expos-

ing gold, lead, and iron, to air and moisture, the iron rusts with great rapidity, the lead is only tarnished, and the gold retains its lustre. It is hence inferred that iron has the greatest affinity for oxygen, lead next, and gold least. This conclusion is supported by concurring observations of a like nature, and confirmed by the circumstances under which the oxides of those metals part with their oxygen. The oxide of silver is reduced by heat only; and the oxide of lead is decomposed by charcoal at a lower temperature than the oxide of iron.

It is inferred from the action of caloric on the carbonates of potash, baryta, lime, and the oxide of lead, that potash has a stronger attraction for carbonic acid than baryta, baryta than lime, and lime than the oxide of lead. The affinity of different substances for water may be determined in a similar manner.

Of all chemical substances, our knowledge of the relative degrees of attraction of the acids and alkalies for each other is the most uncertain. Their action on one another is affected by so many circumstances, that it is in most cases impossible, with certainty, to refer any effect to its real cause. The only methods that have been hitherto devised for remedying this defect are those of Berthollet and Kirwan. Both of them are founded on the capacities of saturation, and the objections which have been urged to the rule suggested by the first philosopher, apply equally to that proposed by the second. But this uncertainty is of no great consequence in practice. We know perfectly the order of decomposition, whatever may be the actual forces by which it is effected.

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## SECTION II.

### *ON THE PROPORTIONS IN WHICH BODIES UNITE, AND ON THE LAWS OF COMBINATION.*

The study of the proportions in which bodies unite naturally resolves itself into two parts. The first includes compounds whose elements appear to unite in a great many proportions; the second comprehends those the elements of which combine in a few proportions only.

I. The compounds contained in the first division are of two kinds. In one, combination takes place unlimitedly in all proportions; in the other, it occurs in every proportion within a certain limit. The union of water with alcohol and the liquid acids, such as the sulphuric, muriatic, and nitric acids, are instances of the first mode of combination; the solutions of salts in water are examples of the second. One drop of sulphuric acid may be diffused through a gallon of water, or a drop of water through a gallon of the acid; or they may be mixed together in any intermediate proportions, and in each case they appear to unite perfectly with one another. A hundred grains of water, on the contrary, will dissolve any quantity of sea-salt which does not exceed forty grains. Its dissolving power then ceases, because the cohesion of the solid becomes comparatively too powerful for the force of affinity. The limit to combination is in such instances owing to the co-

hesive power; and but for the obstacle which it occasions, the salt would most probably unite with the water in every proportion.

All the substances that unite in many proportions, give rise to compounds which have this common character, that their elements are united by a feeble affinity, and preserve, when combined, more or less of the properties which they possess in a separate state. In a scientific point of view, these combinations are of minor importance; but they are exceedingly useful as instruments of research. They enable the chemist to present bodies to one another, under the most favourable circumstances possible for acting with effect; the liquid form is thus communicated to them, while the affinity of the solvent or menstruum, which holds them in solution, is not sufficiently powerful to interfere with their attraction for one another.

II. The most interesting series of compounds is produced by substances which unite in a few proportions only; and which, in combining, lose more or less completely the properties that distinguished them when separate. Of these bodies, some form but one combination. Thus, there is only one compound of zinc and oxygen, or of chlorine and hydrogen. Others combine in two proportions. For example, two compounds are formed by copper and oxygen, or by hydrogen and oxygen. Other bodies again unite in three, four, five, or even six proportions, which is the greatest number of compounds that any two substances are known to produce, excepting those which belong to the first division.

The combination of substances that unite in a few proportions only, is regulated by three remarkable laws. The first of these laws is that the composition of bodies is fixed and invariable; that a compound substance, so long as it retains its characteristic properties, must always consist of the same elements united together in the same proportion. Sulphuric acid, for example, is always composed of sulphur and oxygen in the ratio of 16 parts\* of the former to 24 of the latter: no other elements can form it, nor can its own elements form it in any other proportion. Water, in like manner, is formed of 1 part of hydrogen and 8 of oxygen; and were these two elements to unite in any other proportion, some new compound, different from water, would be the product. The same observation applies to all other substances, however complicated, and at whatever period they were produced. Thus, sulphate of baryta, whether formed ages ago by the hand of nature, or quite recently by the operations of the chemist, is always composed of 40 parts of sulphuric acid and 78 of baryta. This law, in fact, is universal and permanent. Its importance is equally manifest. It is the essential basis of chemistry, without which the science itself could have no existence.

Two views have been proposed by way of accounting for this law. The explanation now universally given of it, is confined to a mere statement, that substances are disposed to combine in those proportions to which they are so strictly limited, in preference to any others; it is regarded as an ultimate fact, because the phenomena are explicable on no other known principle. A different doctrine was advanced by the celebrated Berthollet in his *Statique Chimique*, published in 1803. Having observed the influence of cohesion and elasticity in modifying the action of affinity as already described, he thought he could trace the operations of the same causes in producing the effect at present

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\* By the expression 'parts' I always mean parts by weight.

under consideration. Finding that the solubility of a salt and of a gas in water was limited, in the first by cohesion, and in the second by elasticity, he conceived that the same forces would account for the unchangeable composition of certain compounds. He maintained, therefore, that within certain limits bodies have a tendency to unite in every proportion; and that combination is never definite and invariable, except when rendered so by the operation of modifying causes, such as cohesion, insolubility, elasticity, quantity of matter, and the like. Thus, according to Berthollet, sulphate of baryta is composed of 40 parts of sulphuric acid and 78 of baryta, not because those substances are disposed to unite in that ratio rather than in any other, but because the compound so constituted has a great cohesive power.

These opinions which, if true, would shake the whole science of chemistry to its foundation, were founded on observation and experiment, supported by all the ingenuity of that highly gifted philosopher. They were ably and successfully combated by Proust, in several papers published in the *Journal de Physique*, wherein he proved that the metals are disposed to combine with oxygen and with sulphur only in one or two proportions, which are definite and invariable. The controversy which ensued between these eminent chemists on that occasion, is remarkable for the moderation with which it was conducted on both sides, and has been properly quoted by Berzelius as a model for all future controversialists. How much soever opinion may have been divided upon this important question at that period, the dispute is now at an end. The infinite variety of new facts, similar to those observed by Proust, which have since been established, has proved beyond a doubt that the leading principle of Berthollet is quite erroneous. The tendency of bodies to unite in definite proportions only, is indeed so great as to excite a suspicion that all substances combine in this way; and that the exceptions thought to be afforded by the phenomena of solution, are rather apparent than real; for it is conceivable that the apparent variety of proportion noticed in such cases may arise from the mixture of a few definite compounds with each other.

The second law of combination is still more remarkable than the first. It has given plausibility to an ingenious hypothesis concerning the ultimate particles of matter, called the *atomic theory*. The law itself, however, contains nothing hypothetical, being the pure expression of a fact, first established by Mr Dalton, and subsequently by many other chemists. The nature of it will be at once understood by a simple perusal of the following table:—

Water is composed of	Hydrogen	1	Oxygen	8
Deutoxide of Hydrogen	Do.	1	Do.	16
Carbonic Oxide	Carbon	6	Do.	8
Carbonic Acid	Do.	6	Do.	16
Hyposulphurous Acid	Sulphur	16	Do.	8
Sulphurous Acid	Do.	16	Do.	16
Sulphuric Acid	Do.	16	Do.	24
Nitrous Oxide	Nitrogen	14	Do.	8
Nitric Oxide	Do.	14	Do.	16
Hyponitrous Acid	Do.	14	Do.	24
Nitrous Acid	Do.	14	Do.	32
Nitric Acid	Do.	14	Do.	40

Now it will be perceived, that in all these compounds, the numbers denoting the oxygen, which is attached to a given weight of the

same base, bear a very simple ratio to one another. The deutoxide of hydrogen contains just twice as much oxygen as water does. The oxygen in carbonic acid is double that of carbonic oxide. The oxygen in the compounds of nitrogen and oxygen is in the ratio of 1, 2, 3, 4, and 5. So obvious indeed is this law, that it is observed at once when we compare the result of a few accurate analyses together; and the only subject of surprise is, that it was not discovered before. It is by no means confined to the compounds of combustibles with oxygen. Thus, the sulphur in the two sulphurets of mercury, the chlorine in the two chlorides of mercury, is as 1 to 2. It extends also to the salts. The bicarbonate of potassa, for example, contains twice as much carbonic acid as the carbonate; and the oxalic acid of the three oxalates of potassa is in the ratio of 1, 2, and 4. We must regard it therefore as a general law, the enunciation of which may be stated in the following terms. When two substances, A and B, unite chemically, the quantities of the two bodies must either be equal, or in the ratio of multiples or sub-multiples of each other. It is often called the law of multiples, or of combination in multiple proportion.

Every one who hears this singular law announced for the first time, will naturally inquire if it really holds good in all cases. It may be stated in reply, that the examination of numerous compound bodies leaves no room to question the universality of the law; but that it is impossible from the present condition of the science that every instance should be in accord with it. Two causes are in operation which tend to prevent such perfect coincidence. In the first place, we are not yet acquainted with all possible combinations; and, secondly, our knowledge of the composition of known substances is not always precise;—circumstances which will not excite surprise when it is considered that the science of chemistry itself, and especially the art of making exact analyses, is of very recent origin. The mode in which the first cause operates is obvious; the effect of the second may be illustrated by a few examples. A few years ago chemists were acquainted with only two compounds of sulphur and oxygen, the sulphurous and sulphuric acids; the former of which is composed of 16 sulphur and 16 oxygen, and the latter of 16 sulphur and 24 oxygen. The quantity of oxygen combined with the same weight of sulphur in these compounds is in the ratio of 2 to 3. But this exception to the law of multiples was only apparent, arising from our ignorance of the hyposulphurous acid, a compound which was first noticed by Gay-Lussac in the year 1813. It is composed of 16 parts of sulphur and 8 of oxygen, so that the oxygen in the three compounds is as 1, 2, and 3. Arsenic affords an example of the same kind, in which, however, the anomaly is not yet explained. We know only two combinations of arsenic and oxygen, which are thus constituted:

	<i>Arsenic.</i>	<i>Oxygen.</i>
Arsenious Acid . .	38	16
Arsenic Acid . .	38	24

in which the oxygen is as 2 to 3. But we may confidently expect on two grounds that an oxide of arsenic will hereafter be discovered; first, because there is the analogous case of sulphur to justify such a supposition; and secondly, because arsenic may be expected to form, like the other metals, a salifiable base with oxygen. The three compounds of oxygen and lead are composed of



		Lead.	Oxygen.
Protoxide	. .	104	8
Deutoxide	. .	104	12
Peroxide	. .	104	16

and the proportion of oxygen, therefore, is as 1 :  $1\frac{1}{2}$  : 2. But it is manifest that the discovery of an oxide formed of 104 to 4 of oxygen would at once make these compounds harmonize with Mr Dalton's law.

The third law of combination is fully as remarkable as the preceding and is intimately connected with it. Water and hyposulphurous acid may be adduced by way of illustration. The former is composed of 8 oxygen to 1 hydrogen; the latter of 8 oxygen to 16 sulphur. Now it is singular that the well-known substance, sulphuretted hydrogen, is constituted of 1 hydrogen to 16 sulphur; that is, the quantities of hydrogen and of sulphur which combine with the same quantity of oxygen combine with one another. Again, 40 parts of selenium with 8 of oxygen form the oxide of selenium, and with 1 of hydrogen, seleniuretted hydrogen; 36 parts of chlorine with 8 of oxygen constitute the oxide of chlorine, and with 1 of hydrogen form muriatic acid gas; 16 parts of sulphur combine with 36 of chlorine to form the chloride of sulphur.

It is manifest, from these examples, that bodies unite according to proportional numbers; and hence has arisen the use of certain terms, as Proportion, Combining Proportion, or Equivalent, to express them. Thus the combining proportions of the substances just alluded to are

Hydrogen	. . .	1
Oxygen	. . .	8
Sulphur	. . .	16
Chlorine	. . .	36
Selenium	. . .	40

When one body combines with another in more than one proportion, then the law of multiples, already explained, comes into action. Thus,

	Sulphur.	Oxygen.
Hyposulphurous Acid is composed of	16 or 1 pr. +	8 or 1 pr.
Sulphurous Acid . . . . .	16 or 1 pr. +	16 or 2 pr.
Sulphuric Acid . . . . .	16 or 1 pr. +	24 or 3 pr.

The most common kind of combination is one proportion of one body either with one or with two proportions of another. Combinations of 1 to 3, or 1 to 4, are very uncommon, unless the more simple compounds likewise exist. Ammonia, however, is a singular instance of the reverse. It is composed of 14 parts of nitrogen, and three of hydrogen. Now 14 is the precise quantity of nitrogen that unites with 8 of oxygen, and therefore 14 is considered as one proportion of nitrogen, which is consequently combined with three proportions of hydrogen. It is probable that compounds of 1 to 1, and 1 to 2, will hereafter be discovered, but they are quite unknown at present.

But this law does not apply to elementary substances only, since compound bodies have their combining proportions which may likewise be expressed in numbers. Thus, since water is composed of one proportion or 8 of oxygen, and one proportion or 1 of hydrogen, its combining proportion is 9. The proportion of sulphuric acid is 40, because it is a compound of one proportion or 16 of sulphur, and three proportions or 24 of oxygen; and in like manner, the combining pro-

portion of muriatic acid is 37, because it is a compound of one proportion or 36 of chlorine, and one proportion or 1 of hydrogen. The proportional number of potassium is 40, and as that quantity combines with 8 of oxygen to form potash, the combining proportion of potash is 48. Now when these compounds unite, one proportion of the one combines with one, two, three, or more proportions of the other, precisely as the simple substances do. The hydrate of potash, for example, is constituted of 48 potash and 9 of water, and its combining proportion is consequently  $48 + 9$  or 57. The sulphate of potash is composed of 40 sulphuric acid + 48 potash; and the muriate of the same alkali of 37 muriatic acid + 48 potash. The combining proportion of the former salt is therefore 88, and of the latter 85.

The composition of the salts affords a very neat illustration of this subject; and to exemplify it still further, I subjoin a list of the proportional numbers of a few acids and alkaline bases.

Fluoric Acid	10	Lithia	18
Phosphoric Acid	28	Magnesia	20
Muriatic Acid	37	Lime	28
Sulphuric Acid	40	Soda	32
Nitric Acid	54	Potash	48
Arsenic Acid	62	Strontia	52
		Barytes	78

It will be seen at a glance, that the neutralizing power of the different alkalies is very different; for the proportion of each base expresses the precise quantity required to neutralize a proportion of each of the acids. Thus 18 of lithia, 32 of soda, and 78 of baryta, combine with 10 of fluoric acid, forming the neutral fluates of lithia, soda, and baryta. The same fact is obvious with respect to the acids; for 28 of phosphoric, 40 of sulphuric, and 62 of arsenic acid unite with 28 of lime, forming a neutral phosphate, sulphate, and arseniate of lime.

These circumstances afford a ready explanation of a curious fact, first noticed by the Saxon chemist Wenzel;—when two neutral salts mutually decompose one another, the resulting compounds are likewise neutral. The cause of this fact is now obvious. If 88 parts of neutral sulphate of potash are mixed with 132 of the nitrate of baryta, the 78 baryta unite with the 40 sulphuric acid, and the 54 nitric acid of the nitrate combine with the 48 potash of the sulphate, not a particle of acid or alkali remaining in an uncombined condition.

<i>Sulphate of Potash.</i>		<i>Nitrate of Baryta.</i>	
Sulphuric acid	40	54 Nitric acid	
Potash	48	78 Baryta	
	<hr/>		<hr/>
	88		132

It matters not whether more or less than 88 parts of sulphate of potash are added; if more, a small quantity of sulphate of potash will remain in solution; if less, nitrate of baryta will be in excess; but in either case the neutrality will be unaffected.

The utility of being acquainted with these important laws is almost too manifest to require mention. Through their aid, and by remembering the proportional numbers of a few elementary substances, the composition of an extensive range of compound bodies may be calculated with facility. By knowing that 6 is the combining proportion of carbon and 8 of oxygen, it is easy to recollect the composition of car-

bonic oxide and carbonic acid; the first being 6 carbon+8 oxygen, and the second, 6 carbon+16 oxygen. Forty is the number of potassium, and potash being its protoxide, is composed of 40 potassium+8 oxygen. From these few data, we know at once the composition of the carbonate and bicarbonate of potash. The first is 22 carbonic acid+48 potash; the second, 44 carbonic acid+48 potash. This is done with very little effort of the memory; and the assistance derived from the method will be manifest on comparing it with the common practice of stating the composition in 100 parts.

<i>Carbonic Oxide.</i>		<i>Carbonic Acid.</i>	
Carbon	42.86 . . . . .		27.27
Oxygen	57.14 . . . . .		72.73
<i>Carbonate of Potash.</i>		<i>Bicarbonate of Potash.</i>	
Carbonic acid	31.43 . . . . .		47.83
Potash	68.57 . . . . .		52.17

From the same data, calculations, which would otherwise be difficult or tedious, may be made rapidly and with ease, without reference to books, and frequently by a simple mental process. The exact quantities of substances required to produce a given effect can be determined with certainty, thus affording information which is often necessary to the success of chemical processes, and of vast consequence both in the practice of the chemical arts, and in the operations of pharmacy.

The same knowledge affords a good test to the analyst by which he may judge of the accuracy of his result, and even sometimes correct an analysis which he has not the means of performing with rigid precision. Thus a powerful argument for the accuracy of an analysis is derived from the correspondence of its result with the laws of chemical union. On the contrary, if it form an exception to them, we are authorized to regard it as doubtful, and may hence be led to detect an error, the existence of which might not otherwise have been suspected. If an oxidized body is found to contain one proportion of the combustible with 7.99 of oxygen, then the inference is unavoidable that 8, or one proportion of oxygen would have been the result, had the analysis been perfect. From the same cause, the discovery of a new compound, whether it has been formed by the chemist, or exists as a mineral in the earth, is always interesting; curiosity is excited to ascertain the ratio of its constituents, and see if it be such as reasoning from the established data would have led us to conjecture.

The composition of a substance may sometimes be determined before any analysis has been made of it. When the new alkali lithia was first discovered, chemists did not possess a sufficient quantity of it for determining analytically how much oxygen it contained. But it is known that the neutral sulphates of the alkalies and earths are composed of one proportion of each constituent, and that the oxide contains one proportion of oxygen. If it be found, therefore, by analysis, that the neutral sulphate of lithia is composed of 40 parts of sulphuric acid and 18 of lithia, we conclude, since 40 is one proportion of the acid, that 18 is the equivalent for lithia, and that the oxide is formed of 8 of oxygen and 10 of lithium.

The method of determining the proportional numbers will be anticipated from what has already been said. The commencement is made by carefully analyzing a definite compound of two simple sub-

stances which possess an extensive range of affinity. No two bodies are better adapted for this purpose than oxygen and hydrogen, and that compound is selected which contains the smallest quantity of oxygen. Water is such a substance, and it is therefore regarded as a compound of one proportion of oxygen to one proportion of hydrogen. But analysis proves that it is composed of 8 parts of the former to 1 of the latter, by which the relative weights of their proportions are determined, that of oxygen being eight times heavier than that of hydrogen.

Some compounds are next examined, which contain the smallest proportion of oxygen or hydrogen in combination with some other substance, the quantities of each being the smallest that can unite together. Carbonic oxide with respect to carbon, and sulphuretted hydrogen with respect to sulphur, answer this description perfectly. The former consists of 8 oxygen and 6 carbon; the latter of 1 hydrogen and 16 sulphur. The proportional number of carbon is consequently 6, and of sulphur 16. The proportions of all other bodies may be determined in the same manner.

Since the proportional numbers merely express the relative quantities of different substances which combine together, it is in itself immaterial what figures are employed to express them. The only essential point is, that the relation should be strictly observed. Thus, we may make the combining proportion of hydrogen 10 if we please; but then oxygen must be 80, carbon 60, and sulphur 160. We may call hydrogen 100 or 1000, or if it were desirable to perplex the subject as much as possible, some high uneven number might be selected, provided the due relation between the different numbers is faithfully preserved. But such a practice would effectually do away with the advantage I have ascribed to the use of the proportional numbers, and hence it is the object of every one to employ such simple ones, that their relation may be perceived by mere inspection. As the opinion of different chemists concerning the simplicity of numbers is somewhat at variance, we possess several series of them. Dr Thomson, for example, makes oxygen 1, so that hydrogen is eight times less than unity, or 0.125, carbon 0.75, and sulphur 2. Dr Wollaston, in his scale of chemical equivalents, fixes oxygen at 10, by which hydrogen is 1.25, carbon 7.5, and so on. According to Berzelius, oxygen is 100. And lastly, several other chemists, such as Dalton, Davy, Henry and others, call hydrogen unity, and therefore oxygen 8. One of these series may easily be reduced to either of the others by an obvious and simple arithmetical process; and excepting that of Berzelius, whose numbers are inconveniently high for practice, it is not very material to which of them the preference is given. I have myself adopted the last, because, as it contains no fractional parts, it appears best adapted to the purpose of teaching.

### *On the Atomic Theory of Mr Dalton.*

The brief sketch which has been given of the laws of combination will, I trust, serve to set the importance of this department of chemical science in its true light. It is founded, as will have been seen, on experiment alone, and the laws which have been stated are the pure expression of fact. It is not necessarily connected with any speculation, and may be kept wholly free from it.

The reason why persons, partially acquainted with the subject, have supposed it to be of a hypothetical nature, is sufficiently obvious. It was impossible to reflect on the regularity and constancy with which bodies obey the laws of proportion, without speculating about the cause of that regularity; and consequently, the facts themselves were no sooner noticed than an attempt was made to explain them. Accordingly, when Mr Dalton published his discovery of those laws, he at once incorporated the description of them with his notion of their physical cause; and even expressed the former in language suggested by the latter. Since that period, though several British chemists of eminence, and in particular Dr Wollaston and Sir H. Davy, have recommended and practised an opposite course, both subjects have been but too commonly comprised under the name of atomic theory; and hence it has often happened that beginners have rejected the whole as hypothetical, because they could not satisfactorily distinguish between what was founded on fact and what was conjectural. All such perplexity would have been avoided, and this department of the science have been far better understood, and its value more justly appreciated, had the discussion concerning the atomic constitution of bodies been always kept distinct from what it was intended to explain. When employed in this limited sense, the atomic theory may be discussed in a few words.

Two opposite opinions have long existed concerning the ultimate elements of matter. It is supposed, according to one party, that every particle of matter, however small, may be divided into smaller portions, provided our instruments and organs were adapted to the operation. Their opponents contend, on the other hand, that matter is composed of certain atoms which are of such a nature as not to admit of farther division. These opposite opinions have from time to time been keenly contested, and with variable success, according to the acuteness and ingenuity of their respective champions. But it was at last perceived that no positive data existed capable of deciding the question, and its interest therefore gradually declined. The progress of modern chemistry has revived the general attention to this controversy, by affording a far stronger argument in favour of the atomic constitution of bodies than was ever advanced before, and which I conceive is almost irresistible. We have only in fact to assume with Mr Dalton that all bodies are composed of ultimate atoms, the weight of which is different in different kinds of matter, and we explain at once the foregoing laws of chemical union.

According to this view, every compound is formed by a combination of the atoms of its constituents. An atom of A may combine with 1, 2, 3, or more atoms of B, an arrangement on which depends the law of multiples. If water, for example, is composed of an atom of hydrogen and an atom of oxygen, it follows that every compound of hydrogen with an additional quantity of oxygen must contain 2, 3, or more atoms of oxygen; some multiple, in a word, by a whole number of the quantity of oxygen contained in water. It is equally clear from this view of the composition of water, that the weight of an atom of oxygen is eight times heavier than an atom of hydrogen. The relative weight of the atoms of other substances may be determined in a similar manner. Thus an atom of carbon is six times, an atom of sulphur sixteen times, and an atom of chlorine thirty-six times heavier than an atom of hydrogen; and this explains why they unite with one another in the proportions expressed by those numbers.



What are called the proportional numbers are in fact nothing else but the relative weights of atoms.

No one can suppose that the laws of chemical union are the effect of chance; there must be some cause for them in the nature of the ultimate particles of matter. This cause, as we have just seen, is completely supplied by the supposed atomic constitution of bodies, which accounts for the phenomena in the most beautiful and consistent manner. So perfect, indeed, is the explanation, that the existence of these laws might have been predicted by the aid of the atomic hypothesis, long before they were actually discovered by analysis. But these are not the only arguments which we at present possess in favour of the existence of ultimate indivisible particles of matter. Dr Wollaston, in his paper on the Finite Extent of the Atmosphere, (Philosoph. Trans. for 1822) has defended this side of the question on a new and independent principle, and the proof he has given of the atomic constitution of bodies appears to me decisive.

Some chemists, even without expressly adopting the atomic theory itself, have followed Mr Dalton in the use of the terms *atom* and *atomic weight*, in preference to *proportion*, *combining proportion*, *equivalent*, and others of a like kind. All these appellations, however, have the same signification; and in using the word *atom*, instead of the others, it should be held in mind that it merely denotes the proportions in which bodies unite; that it is the expression of a fact which will remain the same, whether the atomic hypothesis, which suggested the employment of the term, be true or false.

There is one circumstance, which at the first view seems hostile to the supposed atomic constitution of matter. In describing the law of multiples, it was mentioned that the oxygen in the three oxides of lead is in the ratio of 1 :  $1\frac{1}{2}$  : 2; so that if we regard the protoxide as composed of one combining proportion of lead to one proportion of oxygen, the second will contain one proportion and a half, or according to the atomic theory, one atom and a half of oxygen. Now, though the half of a combining proportion may be admitted, the existence of half an indivisible particle of matter is inconceivable; and this circumstance would be fatal to the atomic theory, were there not some satisfactory mode of accounting for it. Several explanations might be brought forward. One of them, as has already been mentioned, rests on the supposition that what is called the protoxide is in reality composed of one atom of lead to two atoms of oxygen, and that the real protoxide has not yet been discovered. Another mode of accounting for the anomaly, is by regarding the present deutoxide as a compound of the protoxide and peroxide combined with one another. A third method is by doubling both elements of the anomalous compound, by which the exact ratio is preserved and the idea of the fraction of an atom avoided. Thus, the protoxide and peroxide of iron are composed, the first of one proportion or 28 metal to 8 of oxygen, and the second of 28 metal to an atom and a half or 12 of oxygen; or what amounts to the same, of 56 or two atoms of iron, to 24 or three atoms of oxygen. These observations prove that the occurrence of half proportions is not inconsistent with the atomic constitution of bodies; they show that the difficulty is explicable, and probably will, during the progress of discovery, be entirely removed. In the mean time, however, it would be inconvenient to allow any speculative notions on the subject to interfere with actual practice, and therefore it is best at once to admit the occurrence of half proportions; and if any

one prefer the term atom to equivalent or proportion, he must submit to the somewhat jarring expression of half an atom.

Mr Dalton supposes that the atoms of bodies are spherical, and has invented certain symbols to represent the mode in which he conceives they may combine together, as illustrated by the following figures.

○ Hydrogen.	○ Oxygen.
⊖ Nitrogen.	● Carbon.

*Binary Compounds.*

○ ○	Water.
○ ●	Carbonic oxide.

*Ternary Compounds.*

○ ○ ○	Deutoxide of hydrogen.
○ ● ○	Carbonic acid.
	&c. &c. &c.

All substances containing only two atoms he called binary compounds, those composed of three atoms ternary compounds, of four, quaternary, and so on.

There are several questions relative to the nature of atoms, most of which will perhaps never be decided. Of this nature are the questions which relate to the actual form, size, and weight of atoms, and to the circumstances in which they mutually differ. All that we know with any certainty is, that their weights do differ, and by exact analysis the relations between them may be determined. The numbers which indicate the combining proportions of bodies are in fact the relative weights of their atoms.

It is but justice to the memory of the late Mr Higgins of Dublin, to state that he first made use of the atomic hypothesis in chemical reasonings. In his "Comparative view of the phlogistic and antiphlogistic theories," published in the year 1789, he observes (pages 36 and 37) that "in volatile vitriolic acid, a single ultimate particle of sulphur is intimately united only to a single particle of dephlogisticated air; and that, in perfect vitriolic acid, every single particle of sulphur is united to two of dephlogisticated air, being the quantity necessary to saturation;" and he reasons in the same way concerning the constitution of water and the compounds of nitrogen and oxygen. These remarks of Mr Higgins do not diminish Mr Dalton's claim of originality. They appear to have been quite unknown to him at the time he published his new system of Chemical Philosophy; and indeed they were made in so casual a manner, as not only to escape observation, but to prove that Mr Higgins himself attached no particular interest to them. Mr Dalton's real merit lies in the discovery of the Laws of Combination, a discovery which is solely and indisputably his; but in which he would have been anticipated by Mr Higgins, had that chemist perceived the importance of his own opinions. The merit of applying the atomic hypothesis to account for these laws likewise belongs to Mr Dalton; nor is his ingenuity in the least affected by the circumstance that another person had previously explained insulated chemical facts on the same principle.

*On the Theory of Volumes.*

Soon after the publication of the New System of Chemical Philoso-

phy in 1808, in which work Mr Dalton explained his views of the atomic constitution of bodies, a paper appeared in the second volume of the *Mémoires d'Arcueil*, by M. Gay-Lussac, on the "Combination of Gaseous Substances with one another." He there proves that gases unite together by volume in very simple and definite proportions. In the combined researches of himself and M. Humboldt, those gentlemen found that water is composed precisely of 100 measures of oxygen and 200 measures of hydrogen; and M. Gay-Lussac, being struck by this peculiarly simple proportion, was induced to examine the combinations of other gases, with the view of ascertaining if any thing similar occurred in other instances.

The first compounds which he examined were those of ammoniacal gas with muriatic, carbonic, and fluoboric acid gases. 100 volumes of the alkali combined with precisely 100 volumes of muriatic acid gas, and they could be made to unite in no other ratio. With both the other acids, on the contrary, two distinct combinations were possible. These are

100	Fluoboric acid gas with	100	Ammoniacal gas.
100	do.	200	do.
100	Carbonic acid gas	100	do.
100	do.	200	do.

Various other examples were quoted, both from his own experiments and from those of others, all demonstrating the same fact. Thus ammonia was found by M. A. Berthollet to consist of 100 volumes of nitrogen and 300 volumes of hydrogen. 100 volumes of sulphurous acid and 50 volumes of oxygen produced sulphuric acid. Carbonic acid is composed of 50 volumes of oxygen and 100 volumes of carbonic oxide.

From these and other instances M. Gay-Lussac established the fact, that gaseous substances unite in the simple ratio of 1 to 1, 1 to 2, 1 to 3, &c.; and this original observation has been confirmed by such a multiplicity of experiments, that it may be regarded as one of the best established laws in chemistry. Nor does it apply to the true gases merely, but to vapours likewise. For example, sulphuretted hydrogen, sulphurous acid, and hydriodic acid gases are composed of

100 vol.	hydrogen and	100 vol.	vapour of sulphur.
100	oxygen	100	. . sulphur.
100	oxygen	100	. . iodine.

There are very good grounds to suppose, also, that solid bodies which are fixed in the fire would, when in the form of vapour, be subject to the same law. By a method which will be explained afterwards, we may calculate what the specific gravity of carbon would be, if converted into vapour; and 0.4166 is the number so determined, atmospheric air being unity. Now, if we assume that carbonic acid is formed of 100 volumes of oxygen, and 100 volumes of the vapour of carbon, condensed into the space of 100 volumes, the specific gravity of carbonic acid will be 1.1111 (the sp. gr. of oxygen) + 0.4166 = 1.5277, which is the precise number determined by experiment. Again, it follows from our assumption, that carbonic acid is composed by weight of

Oxygen	1.1111	.	.	16 or 2 prop.
Carbon	0.4166	.	.	6 or 1 prop.

as ascertained by analysis.

If we assume that carbonic oxide is composed of 50 volumes of oxygen and 100 volumes of the vapour of carbon, condensed into the space of 100 volumes, then its specific gravity will be 0.5555 (half the sp. gr. of oxygen)  $+ 0.4166 = .9721$ ; and its composition will be

Oxygen	0.5555	.	.	8 or 1 prop.
Carbon	0.4166	.	.	6 or 1 prop.

both of which results have been determined by other methods.

The compounds of carbon and hydrogen are equally illustrative of the same point. If light carburetted hydrogen is formed of 200 volumes of hydrogen and 100 volumes of the vapour of carbon, condensed into 100 volumes, its specific gravity should be 0.1388 (twice the sp. gr. of hydrogen)  $+ 0.4166 = 0.5554$ ; and its composition by weight will be

Hydrogen	.	0.1388	.	2
Carbon	..	0.4166	.	6

If olefant gas is composed of 200 volumes of hydrogen and 200 volumes of the vapour of carbon, its specific gravity will be 0.1388  $+ 0.8332 = 0.9720$ ; and its composition by weight must be

Hydrogen	.	0.1388	.	2
Carbon	.	0.8332	.	12

I need hardly observe that both these results have been ascertained by analysis.

Another remarkable fact established by M. Gay-Lussac in the same paper is, that the diminution of bulk which gases frequently suffer in combining, is also in a very simple ratio. Thus, the 4 volumes of which ammonia is constituted, (3 volumes of hydrogen and 1 of nitrogen) contract to one-half or two volumes when they unite. There is a contraction to two-thirds in the formation of nitrous oxide gas. The same applies to the combination of gases and vapours. There is contraction to a half in the formation of sulphuretted hydrogen; and to a half in that of sulphurous acid. The instances just quoted relative to the vapour of carbon confirm the same remark. There is a contraction to two-thirds in carbonic oxide; to a half in carbonic acid; to a third in light carburetted hydrogen; and to a fourth in olefant gas.

The rapid progress which chemistry has made within the last few years is in a great measure attributable to the ardour with which pneumatic chemistry has been cultivated. That very department which at first sight appears so obscure and difficult, has afforded a greater number of leading facts than any other; and the law of Gay-Lussac, by giving an additional degree of precision to such researches, as well as from its own intrinsic value, is one of the brightest discoveries that adorn the annals of the science. The practice of estimating the quantity in weight of any gas, by measuring its bulk or volume, of itself susceptible of much accuracy, is rendered still more precise and satisfactory by the operation of this law. It will not perhaps be superfluous, therefore, to exemplify the method of reasoning employed in these investigations by a few examples; which will serve, moreover, as a useful specimen to the beginner of the nature of chemical proof.

One essential element in every inquiry of this kind, which is indeed the keystone of the whole, is a knowledge of the specific gravity of the gases. But it is exceedingly difficult to determine the specific gra-

vity of gases with perfect accuracy; for not only do slight alterations of temperature and pressure during the experiment affect the result, but the presence of a little watery vapour, atmospheric air, or other impurity, may cause a material error, especially when the gas to be weighed is either very light or very heavy. The specific gravity of important gases has, accordingly, been stated differently by different chemists, and there is none in regard to which more discordant statements of this fact have been made than of hydrogen gas. Fortunately we possess the power of correcting the results, and of estimating their accuracy by means of other data, upon which greater reliance may be placed. According to our best data, the specific gravity of oxygen, hydrogen, and nitrogen gases, air being 1, is

Oxygen	.	.	1.1111
Hydrogen	.	.	0.0694
Nitrogen	.	.	0.9722

It has been proved by analysis that 200 volumes of ammoniacal gas are composed of 300 volumes of hydrogen and 100 volumes of nitrogen, from which the specific gravity of that alkali may be calculated.

$$\text{Thus, } 0.9722 + (0.0694 \times 3) = 1.1804.$$

$$\frac{1.1804}{4} = 0.2951 \text{ which is the specific gravity ammoniacal gas}$$

should have, did its constituent gases suffer no contraction; but as they contract to one-half, the real specific gravity is double what it otherwise would be, or is 0.5902. Now, if by weighing a certain quantity of ammoniacal gas, the same number is procured for its specific gravity, it follows that all the elements of the calculation must have been correct.

Nitric oxide is composed of 100 volumes of nitrogen and 100 volumes of oxygen, united without any contraction, and forming, consequently, 200 volumes of the compound. Its specific gravity must, therefore, be the mean of its components, or  $\frac{1.1111 + 0.9722}{2} = 1.0416$ .

The coincidence of this calculated result with that determined by weighing the gas itself, proves that all the data are true. It is obvious, indeed, that the calculated results, as being free from the unavoidable errors of manipulation, must be the most accurate, provided the elements of the calculation may be trusted.

Dr Henry has proved by careful analysis that 100 volumes of light carburetted hydrogen gas, a compound of carbon and hydrogen, require 200 volumes of oxygen for complete combustion; that water and carbonic acid are the sole products; and that the latter amounts precisely to 100 volumes. From these data, the proportions of its constituents and its specific gravity may be determined. For 100 volumes of carbonic acid contain 100 volumes of the vapour of carbon, which must have been present in the carburetted hydrogen, and 100 volumes of oxygen. One half of the oxygen originally employed is thus accounted for; and the remainder must have combined with hydrogen. But 100 volumes of oxygen require 200 volumes of hydrogen for combination, all of which must likewise have been contained in the carburetted hydrogen. The 100 volumes of light carburetted hydrogen, submitted to analysis, are hence composed of 100 volumes of the vapour of



carbon, and 200 volumes of hydrogen. Its specific gravity must therefore be 0.5554, that is, 0.4166 (the sp. gr. of carbon vapour)  $\div 0.1388$  or twice the sp. gr. of hydrogen gas.

Having ascertained that light carburetted hydrogen gas is composed of two measures of hydrogen to one of the vapour of carbon, it is easy to calculate the proportion of its constituents in weight. For this purpose we need only multiply the bulk of the gases by their respective specific gravities. Thus  $200 \times 0.0694 = 13.88$ , and  $100 \times 0.4166 = 41.66$ . Hence light carburetted hydrogen is composed by weight of

Carbon	:	:	41.66	:	6
Hydrogen	:	:	13.88	:	2

The theory of volumes has very considerable analogy to Mr Dalton's law of multiple proportions. The former is indeed, to a certain extent, a consequence of the latter; for if one body unites with another in several proportions, the quantities of the variable ingredient will stand in the same relation to one another, when expressed by volume, as they do by weight. But there is one remarkable difference. The weights of the two elements of a compound have no apparent dependence on one another. Thus, 6 carbon and 8 oxygen form carbonic oxide; 8 oxygen and 14 nitrogen form nitrous oxide; 8 is no multiple by any whole number of 6, nor 14 of 8. But the elements of a compound are always united by volume in the ratio of 1 to 1, 1 to 2, 1 to 3, and so on. This distinction is certainly very obvious; but still there is otherwise such a similarity in the two laws, that the peculiar nature of the ultimate particles of matter which gives rise to the one, must surely be the cause of the other. It is to be hoped, therefore, that the connecting link will soon be supplied, and one fact of great interest has been already determined, which may ultimately be of use in accounting for this difference. In the 6th volume of the *Annals of Philosophy*, (old series) Dr Prout published an essay "On the Relation between the Specific Gravities of Bodies in their Gaseous state and the Weights of their Atoms," in which he showed that the atomic weights, or equivalents of several substances, are multiples by a whole number of the atomic weight of hydrogen gas. Dr Thomson took up this idea, and in his recent admirable treatise on the "First Principles of Chemistry," has proved that it applies generally; that the atomic weights of all the simple substances he has examined are not only multiples by a whole number of the atomic weight of hydrogen, but with very few exceptions of two atoms of hydrogen.

Dr Prout pointed out another circumstance of much interest with respect to this question, in the paper above alluded to. He showed that in general the specific gravity of a body in its gaseous state, may be obtained by multiplying its atomic weight (the atom of oxygen being taken as unity) by 0.5555, or half the specific gravity of oxygen gas; and Dr Thomson, in the 7th chapter of the work just mentioned, has discussed the subject at considerable length. The following explanation will, I hope, make the reason of this rule intelligible. Water is composed of one volume of oxygen to two volumes of hydrogen; and as chemists regard it as a compound of one atom of each element, it of course follows that one atom of hydrogen must occupy twice the space of an atom of oxygen. It would be exceedingly convenient, did the atoms of different bodies occupy the same space when in the gaseous form; for then the atoms would be represented by volumes,

and the numbers which express the relative weights of the former, would be identical with the specific gravity of the gases. But it has been already stated, that an atom of oxygen occupies one half the bulk of an atom of hydrogen; and it follows therefore that the specific gravity of the former gas must be twice as great as it would be, did it occupy the same space as the latter. Hence the rule, as

$$1 \quad : \quad 0.125 \quad : : \quad 0.5555 \quad : \quad 0.0694$$

in which 1 is the atomic weight of oxygen; 0.125 the atomic weight of hydrogen; 0.5555 half the specific gravity of oxygen gas; and 0.0694 the fourth proportional, the specific gravity of hydrogen.

The atoms of several other substances besides hydrogen, occupy in the gaseous state twice the space of an atom of oxygen; indeed, as far as is yet known, every simple substance, though naturally solid, is in this condition, besides the majority of compound gases; and in all such instances, it is easy to calculate the specific gravity of a body by multiplying its atomic weight by 0.5555, or half the specific gravity of oxygen\*.

It appears at first sight to be an easy matter to make the atoms and volumes of bodies correspond to one another; and that it might be effected by considering water as a compound of an atom of oxygen to two atoms of hydrogen. Sir H. Davy has accordingly done so in his *Elements of Chemical Philosophy*, and the atom of oxygen will therefore be 16, that of hydrogen being unity. But the inconvenience arising from this practice is far greater than the evil it was intended to remedy. For, on this supposition, sulphuretted hydrogen must be held as an atom of sulphur with two atoms of hydrogen, while it is composed of one volume of each of its constituents. Muriatic acid gas would consist of one atom of chlorine, and two atoms of hydrogen, though formed of one volume of each gas. The same remark applies to hydriodic acid, hydrocyanic acid, and most other compound gases containing hydrogen.

The reason of this is, that the atoms and volumes of all the simple gases, (oxygen excepted) and many compound ones also, according to the received system, correspond with one another. Sulphuretted hydrogen is composed of one volume or one atom of sulphur to one volume or one atom of hydrogen. Muriatic acid is composed, in like manner, of one volume or one atom of its constituents. Light carburctted hydrogen is a compound of two volumes of hydrogen to one volume of the vapour of carbon, or of two atoms of hydrogen to one of carbon. All this advantage is lost by regarding water as a compound of two atoms of hydrogen to one of oxygen; and this forms a sufficient reason for not adopting the method of Sir H. Davy.

### *On the Theory of Berzelius.*

It is well known that the celebrated Professor of Stockholm has for many years devoted himself to the study of the laws of definite pro-

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\* This rule applies only when the weight of the atom is expressed according to the oxygen scale. If hydrogen is represented by unity, then the rule is to multiply 0.5555 by the atomic weight of the body, and divide by 8,—the atomic weight of oxygen.

portions, and that he has been led to form a peculiar hypothesis, by way of generalizing the facts which his industry had collected. To give a detailed account of his system, does not fall within the plan of this work ; to treat of the atomic theory without alluding to the labours of Berzelius, would, on the other hand, be inexcusable: I shall adopt a middle course, by stating briefly the principal opinions of that eminent chemist, offering at the same time a few comments upon them.

Berzelius informs us in the historical introduction to his treatise on the "Theory of Definite Proportions," that he commenced his researches on the subject in the year 1807 ; and that they originated in the study of the Works of Richter. From Richter's explanation of the fact, that when two neutral salts decompose one another, the resulting compounds are likewise neutral, he perceived that one good analysis of a few salts would furnish the means of calculating the composition of all others. He accordingly entered upon an inquiry, which was at first limited in its object ; but as he proceeded, his views enlarged, and advancing from one step to another, he at length set about determining the laws of combination in general. In perusing his account of the investigation, we are at a loss whether most to admire the number of exact analyses which he performed, the variety of new facts he determined, his acuteness in detecting sources of error, his ingenuity in devising new analytical processes, or the persevering industry which he displayed in every part of the inquiry. But it is at the same time impossible to suppress regret, that, instead of forming a complex system of his own, he did not adopt the simple views of Mr Dalton. This he might have done with very great propriety ; since the fundamental laws which he discovered, are, with very little exception, either identical with those previously pointed out by the British Philosopher, or the direct result of their operation.

Berzelius assumes, with Mr Dalton, the existence of ultimate indivisible atoms, to the combination of which with one another the laws of chemical proportion are owing.

The first law of Berzelius is the following. "One atom of one element unites with 1, 2, 3, or more atoms of another element." This is the grand law of Mr Dalton, and requires no comment, further than that it has been amply confirmed by the labours of Berzelius. The second is, that "two atoms of one element combine with three atoms of another." These are the two laws which regulate the union of simple or elementary atoms.

The combination of compound atoms with each other, obeys another law, and is confined within still narrower limits. "Two compounds which contain the same electro-negative body, always combine in such a manner that the electro-negative element of the one is a multiple by a whole number of the same element of the other." Thus, for instance, if two oxidized bodies unite, the oxygen of one is a multiple by a whole number of the oxygen in the other. Various examples may be given of this. The hydrate of potash is composed of

Potash	48,	the oxygen of which is	8.
Water	9,	do.	8.

In like manner, if two acids or two oxides combine, the same will be observed.

In the earthy minerals which often contain several oxides, the same law is found to prevail with great uniformity.

The composition of the salts is likewise under its influence. Carbonate of potash, for example, is composed of

Carbonic acid 22, the oxygen of which is 16.  
Potash . 48, do. 8.

and sulphate of potash of

Sulphuric acid 40, the oxygen of which is 24.  
Potash . 48, do. 8.

Berzelius has remarked, that the nitrates, phosphates, and arseniates, may prove exceptions to the law in some instances. There is also a similar relation in salts which contain water of crystallization, between the oxygen of the base of the salt and that of the water. For instance, crystallized sulphate of soda is composed of

Sulphuric acid 40.  
Soda . 32, the oxygen of which is 8.  
Water . 90, do. 80.

Double salts are also influenced by the same law. In the tartrate of potash and soda, for example, the oxygen of the potash is exactly equal to the oxygen in the soda; and the oxygen in the tartaric acid, which neutralizes the potash, is equal to that of the soda.

But this is not all that Berzelius has remarked with respect to the constitution of the salts. He observes that in each series of salts, the same relation always exists between the oxygen of the acid and of the base. In all the neutral sulphates this ratio is as one to three, as may be seen in the sulphates of soda and potash. In the carbonates, the oxygen of the acid is double; and in the bicarbonates quadruple the oxygen of the base.

The existence of these remarkable laws was discovered by Berzelius at a very early period of his researches; and he mentions, that as subsequent observation, during the course of several years, has not afforded a single exception to them, he now regards them as universal. He accordingly places unlimited confidence in their accuracy, and is in the constant habit of calculating the composition of bodies on this principle.

It will of course be interesting to inquire into the cause of these phenomena; to ascertain if there is any property peculiar to oxygen, or other negative electrics, which might give rise to them. Berzelius himself says that "the cause is involved in such deep obscurity, that it is impossible at the present moment to give a probable guess at it." I have the misfortune to differ entirely from Berzelius on this question. So far from being obscure, it is perfectly intelligible, and is precisely what might have been anticipated from the present state of chemical knowledge. Most of the salts called neutral sulphates, are composed of one proportion or one atom of sulphuric acid, and one atom of some protoxide. This is the case with all the alkaline and earthy sulphates and with several of the common metals, as lead, zinc, and iron. Now, an atom of sulphuric acid is composed of

Sulphur 16—1 atom.  
Oxygen 24—3 atoms.

and every protoxide of

Metal —1 atom.  
Oxygen 8—1 atom.

Hence a number of laws may be deduced which must hold in every sulphate of a protoxide.

1. The oxygen of the acid is a multiple of that of the base.
2. The acid contains three times as much oxygen as the base.
3. The sulphur of the acid is just double the oxygen of the base.
4. The acid itself is five times as much as the oxygen of the base.

Metallic sulphurets are frequently composed of an atom of each element; and should oxidation ensue, so that the sulphur is converted into sulphuric acid, and the metal into a protoxide, they will be in the exact proportion for forming a neutral sulphate. Berzelius has proved by analysis that this happens frequently, and he is disposed to convert it into a general law.

Again, the carbonates are composed of one atom of carbonic acid, and one atom of some protoxide. But an atom of carbonic is composed of

Carbon 6, 1 atom.  
Oxygen 16, 2 atoms.

and every protoxide of

Metal —1 atom.  
Oxygen 8, 1 atom.

It is inferred, therefore, that in all the carbonates, the oxygen of the acid is exactly double that of the base; and the same mode of reasoning is applicable to the various genera of salts. These few examples will suffice to show, that what seemed so obscure to Berzelius, is rendered quite obvious by the Daltonian method. We perceive, moreover, that no constant ratio can exist between the quantity of oxide and that of the acid or oxygen of the acid; and the reason is, because the atomic weights of the metals are different. But this view of the subject answers another useful purpose; it enables us to see whether the law of Berzelius is or is not universal. The observations made on this subject by Dr Thomson, in his "First Principles of Chemistry," are so much to the point, that I cannot do better than give them in his own words.

"Before concluding these general observations," says Dr Thomson, "I may say a few words on Berzelius' law, that in all salts, the atoms of oxygen in the acid constitute a multiple by a whole number of the atoms of oxygen of the base. This law was founded upon the first set of exact analyses of neutral salts which Berzelius made. Now, as neutral salts in general are combinations of an atom of a protoxide with an atom of an acid, it is obvious that the atoms of oxygen in the acid must in all such salts be multiples of the atom of oxygen in the base; because every whole number is a multiple of unity. Neutral salts, therefore, are not the kind of salts by means of which the precision of this supposed law can be put to the test."

"Even in the subsalts, composed of 1 atom of acid united to 2 atoms of base, it is obvious enough that the law will hold whenever the acid combined with the base happens to contain 2 or 4, or any even number of atoms; because all even numbers are multiples of 2. Now, this is the case with the following acids:

Phosphoric.	Nitrous.	Antimonic.	Citric.
Carbonic.	Titanic.	Manganesic.	Sacclactic.
Boracic.	Arsenious.	Molybdous.	Chromous.
Sulphurous.	Selenic.	Uranitic.	



Consequently, the law must hold good in all combinations of 1 atom of these acids with 2 atoms of base."

"In the case of all these acids which contain only one atom of oxygen, all the subsalts composed of 1 atom of the acid united to 2 atoms of base, the law will also in some sort hold; for the atoms of the oxygen in such acids being 1, this number will always be a submultiple of 2, the number of atoms of oxygen in 2 atoms of base. This is the case with the following acids:

Silicic.  
Phosphorous.

Hypo-sulphurous.  
Oxide of Tellurium.

"It is only in the subsalts of acids containing an odd number of atoms of oxygen, that exceptions to the law can exist. It is to them, therefore, that we must have recourse when we wish to determine whether this empirical law of Berzelius be founded in nature or not. Now, there are 13 acids, the integrant particles of which contain an odd number of atoms of oxygen. The following table exhibits the names of these acids, together with the number of atoms of oxygen in each."

<i>Atoms of Oxygen.</i>				<i>Atoms of Oxygen.</i>			
Sulphuric acid	.	.	3	Acetic acid	.	.	3
Arsenic	.	.	3	Succinic	.	.	3
Chromic	.	.	3	Benzoic	.	.	3
Molybdic	.	.	3	Nitric	.	.	5
Tungstic	.	.	3	Tartaric	.	.	5
Oxalic	.	.	3	Hypo-sulphuric	.	.	2½
Formic	.	.	3				

Dr Thomson informs us that the number of subsalts he has examined is exceedingly small, because his "object was not to investigate the truth of Berzelius' law, but to determine the quantity of water of crystallization which the salts contain." He observes, that "it would certainly be a most remarkable circumstance if 2 atoms of any protoxide were incapable of combining with 1 atom of any of the 13 acids in the preceding list." Dr T. adduces seven instances in which this does happen, three of which are completely in point, being a sub-sulphate of alumina, a subacetate of lead, and a subacetate of copper; and he is "persuaded that many more will be discovered whenever the attention of chemists is particularly turned to the subsalts." He also mentions other kinds of salts, in regard to which, for equally obvious reasons, the law cannot and does not hold.

These extracts will suffice for placing the law of Berzelius in its true light; for showing that it is a direct consequence of the general operation of the Laws of Definite Proportion; and that we must expect to find some exceptions to his law, derived from the very cause which gives rise to it. It is to be hoped that Berzelius will take the remarks of Dr Thomson into mature consideration, by which he will probably perceive that his favourite canon is not so universal as he imagines, and be led to avoid the errors to which, from an indiscriminate employment of it, both himself and his pupils might otherwise be exposed.

That part of the law which applies to the combined water is likewise more than doubtful. When the base contains 2 atoms of oxygen and an uneven number of atoms of water is present, it cannot be correct. When the base contains 3 atoms of oxygen, the law would not apply whenever there chanced to be 2, 4, 8, or 10 atoms of water.

When the base has only one atom of oxygen, then it must hold for obvious reasons. When the base has an atom and a half of oxygen, the law can only be true when 3, 6, 9, or 12 atoms of water are in combination; with 1, 2, 4, 5, 7, 8, or 10, it must fail. The hydrate of the peroxide of iron is an exception of this kind, and similar ones are to be looked for among the crystallized salts of the peroxide.

An admirable attempt has been made within these few years to determine the atomic constitution of minerals, in which Berzelius has highly distinguished himself. The composition of minerals must of course be influenced by the usual laws of combination, though there are sometimes obstacles in the way of discovering it. In the compounds made artificially, chemists possess the power of having each constituent perfectly pure; but, unfortunately, we cannot always command the same condition with respect to natural productions. The materials of which a mineral is composed, once formed a part of some heterogeneous fluid or semi-fluid mass, and in assuming the solid form are very likely to have enclosed within them some substance which does not, chemically considered, form a part of the mineral. The result of chemical analysis, accordingly, does not always give us a view of the actual constitution of a mineral species; some substances are often detected which are foreign to it, and the chemist must exercise his judgment in determining what is and what is not essential. Now nothing is so well calculated to direct him as a knowledge of the laws of combination; but as a great discretionary power is in his hands, it is important that his mode of investigation should be the simplest possible, and that his rules should be founded on well established principles, which involve nothing hypothetical. It is but very lately that due care has been bestowed in selecting sufficiently pure specimens for examination, or in performing the analyses themselves with the precision necessary for determining the chemical constitution of minerals. It were much to be wished that our first essays in this difficult field should be confined as much as possible to such minerals as contain but few substances, and which occur in distinct transparent crystals.

We are indebted to Berzelius for this mode of studying the composition of minerals; and certainly if skill in analytical investigation could encourage any one to make the attempt, none could undertake it with greater chance of success than the indefatigable Professor of Stockholm. Unfortunately his theoretical views are unnecessarily complex, and I much doubt, for reasons already stated, if his ruling law about multiples of oxygen deserves the confidence he bestows upon it. It will not, I am convinced, be adopted by the chemists and mineralogists of this country, and I am much mistaken if, notwithstanding the great reputation of its author, it stand its ground long upon the continent. To give a particular description of his method is foreign to my purpose, but the reader will find an able account of it in the 9th vol. of the *Annals of Philosophy*, N. S. by Mr Children.

## SECTION III.

## OXYGEN.

Oxygen gas was discovered by Priestley in 1774, and by Scheele a year or two after, without previous knowledge of Priestley's discovery. Several appellations have been given to it. Priestley named it *De-phlogisticated air*; it was called *Empyreal air* by Scheele, and *Vital air* by Condorcet. The name it now bears, derived from the Greek words *οξύς acid*, and *γεννᾶω I generate*, was proposed by Lavoisier, from the supposition that it was the whole cause of acidity.

Oxygen gas may be obtained from several sources. The peroxides of manganese, lead, and mercury, nitre, and the chlorate of potash, all yield it in large quantity when they are exposed to a red heat. The substances commonly employed for the purpose are the peroxide of manganese and the chlorate of potash. It may be procured from the former in two ways; either by heating it to redness in a gun-barrel, or in a retort of iron or earthen-ware; or by putting it into a flask with half its weight of concentrated sulphuric acid, and heating the mixture by means of a lamp. To understand the theory of these processes, it is necessary to be aware that there are three distinct oxides of manganese, which are thus constituted:

*Manganese.*

Protoxide	.	28 or one prop.	+	8	.	=	36
Deutoxide	.	28	.	+	12	.	= 40
Peroxide	.	28	.	+	16	.	= 44

On applying a red heat to the last, it parts with half a proportion of oxygen, and is converted into the deutoxide. Every 44 grains of the peroxide will therefore lose, if quite pure, 4 grains of oxygen, or nearly 12 cubic inches; and one ounce will yield about 128 cubic inches of gas. The action of sulphuric acid is different. The peroxide loses a whole proportion of oxygen, and is converted into the protoxide, which unites with the acid, forming a sulphate of the protoxide of manganese. Every 44 grains of the peroxide must consequently yield 8 grains of oxygen and 36 of the protoxide, which, by uniting with one proportion (40) of the acid, forms 76 of the sulphate. The first of these processes is the most convenient in practice.

The gas obtained from the peroxide of manganese, though hardly ever quite pure, owing to the presence of carbonate of lime, is sufficiently good for ordinary purposes. It yields a gas of better quality, if previously freed from the carbonate of lime by dilute muriatic or nitric acid; but when oxygen of great purity is required, it is better to obtain it from the chlorate of potash. For this purpose, the salt should be put into a retort of green glass, or of white glass made without lead, and be heated nearly to redness. It first becomes liquid, though quite free of water, and then, on an increase of heat, is wholly resolved into pure oxygen gas, which escapes with effervescence, and into a white compound, called the chloride of potassium, which is left in the retort. The theory of the decomposition is as follows. The chlorate of potash is composed of

Chloric acid 76 or one proportion.  
Potash 48 or one proportion.

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124

Chloric acid consists of

Chlorine 36 or one proportion.  
Oxygen 40 or five proportions.

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76

and potash of

Potassium 40 or one proportion.  
Oxygen 8 or one proportion.

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48

The chlorine and potassium are both deprived of their oxygen, and then unite together. So that 124 grains of the salt are resolved into 76 grains of the chloride of potassium, and 48 grains, or 141 cubic inches, of pure oxygen.

Oxygen gas is colourless, has neither taste nor smell, is not chemically affected by the imponderables, refracts light very feebly, and is a non-conductor of electricity. It is the most perfect negative electric that we possess, always appearing at the positive pole when any compound which contains it is exposed to the action of galvanism. It emits light, as well as heat, when suddenly and forcibly compressed.

Oxygen is heavier than atmospheric air. Chemists have differed as to its precise weight; but the late experiments of Dr Thomson, (First Principles of Chemistry,) leave little doubt of the accuracy of Dr Prout's estimate as stated in the 6th volume, O. S. of the Annals of Philosophy. According to that chemist, 100 cubic inches of oxygen, when the thermometer is at 60° F. and the barometer stands at 30 inches, weigh 33.888 grains, and its specific gravity must be 1.1111.

Oxygen gas is very sparingly absorbed by water, 100 cubic inches of that liquid dissolving only three or four of the gas. It has neither acid nor alkaline properties; for it does not redden or turn green the blue vegetable colours, nor does it evince a disposition to unite either with acids or alkalies. It has a very powerful attraction for most of the simple bodies; and there is not one of them with which it may not be made to combine. The act of combining with oxygen is called *oxidation*, and the bodies, after having united with it, are said to be *oxidized*. The compounds so formed are divided by chemists into acids and oxides. The first division includes those compounds which possess the general properties of acids; and the second comprehends those in which that character is wanting. The phenomena of oxidation are variable. It is sometimes produced with great rapidity, and with an evolution of heat and light. Ordinary combustion, for instance, is nothing more than rapid oxidation; and all inflammable or combustible matters derive their power of burning in the open air from their affinity for oxygen. On other occasions it takes place slowly, and without any appearance either of heat or light, as is exemplified by the rusting of iron when exposed to a moist atmosphere. Different as these processes may appear, oxidation is the result of both; and both are owing to the same circumstance, namely, to the presence of oxygen in the atmosphere.

All substances that are capable of burning in the open air, burn with far greater brilliancy in oxygen. A piece of wood, on which the least spark of light is visible, bursts into flame the moment it is put into a jar of oxygen; lighted charcoal emits beautiful scintillations; and phosphorus burns with so powerful and dazzling a light that the eye cannot bear its impression. Even iron and steel, which are not commonly ranked among the inflammables, undergo a rapid combustion in oxygen gas.

The changes that accompany these phenomena are no less remarkable than the phenomena themselves. When a lighted taper is put into a vessel of oxygen gas, it burns for a while with increased splendour; but the size of the flame soon begins to diminish, and if the mouth of the jar be properly secured by a cork, the light will in a short time disappear entirely. The gas has now lost its characteristic property; for a second lighted taper, immersed in it, is instantly extinguished. This result is general. The burning of one body in a given portion of oxygen unfits it for supporting the combustion of another; and the cause of it is manifest. The combustion is produced by the combination of inflammable matter with oxygen gas. The quantity of free oxygen, therefore, diminishes during the process, and is at length exhausted. The burning of all bodies, however inflammable, must then cease, because the presence of oxygen is necessary to its continuance. For this reason oxygen gas is called a supporter of combustion. The oxygen often loses its gaseous form as well as its properties. If phosphorus or iron be burned in a jar of pure oxygen over water or mercury, the disappearance of the gas becomes obvious by the ascent of the liquid, which is forced up by the pressure of the atmosphere, and fills the vessel. Sometimes, on the contrary, the oxygen suffers only a partial diminution of volume, or even undergoes no change of bulk at all, as is exemplified by the combination of the diamond.

The changes experienced by the burning body are equally striking. While the oxygen loses its power of supporting combustion, the inflammable substance lays aside its combustibility. It is now an oxidized body, and cannot be made to burn even by the aid of the purest oxygen. It has also acquired an addition to its weight. It is an error to suppose that bodies lose any thing while they burn. The materials of our fires and candles do indeed disappear, but they are not destroyed. Although they fly off in the gaseous form, and are commonly lost to us, it is not difficult to collect and preserve all the products of combustion. When this is done with the requisite care, it is constantly found that the combustible matter weighs more after than before combustion; and that the increase in weight is exactly equal to the quantity of oxygen which has disappeared during the process.

Oxygen is necessary to respiration. No animal can live in an atmosphere which does not contain a certain portion of uncombined oxygen; for an animal soon dies if put into a portion of air from which the oxygen has been previously removed by a burning body. It may therefore be anticipated that oxygen is consumed during respiration. If a bird be confined in a limited quantity of atmospheric air it will at first feel no inconvenience; but as a portion of oxygen is withdrawn at each inspiration, its quantity diminishes rapidly, so that respiration soon becomes laborious, and in a short time ceases altogether. Should another bird be then introduced into the same air, it will die in



the course of a few seconds; or if a lighted candle be immersed in it, its flame will be extinguished. Respiration and combustion have therefore the same effect. An animal cannot live in an atmosphere which is unable to support combustion; nor can a candle burn in air which is unfit for respiration.

### *On the Theory of Combustion.*

Two meanings are attached to the term *combustion*. In its old signification it means the combination of combustible matter with oxygen gas under evolution of heat and light. According to recent usage it is extended to many instances of chemical action where heat and light make their appearance. I shall employ the term at present in its former sense.

For many years prior to the discovery of oxygen, the phenomena of combustion were explained on the Stahlian or phlogistic hypothesis. All combustible bodies, according to Stahl, contain a certain principle which he called *phlogiston*, to the presence of which he ascribed their combustibility. He supposed that when a body burns, phlogiston escapes from it; and that when a body has lost phlogiston, it ceases to be combustible, and is then a dephlogisticated or incombustible substance. A metallic oxide was consequently regarded as a simple substance, and the metal itself as a compound of its oxide with phlogiston. The heat and light which accompany combustion were attributed to the rapidity with which phlogiston is evolved during the process.

The discovery of oxygen proved fatal to the Stahlian doctrine. Lavoisier had the honour of overthrowing it, and of substituting in its place the antiphlogistic theory. The basis of his doctrine has already been stated;—that combustion and oxidation in general consist in the combination of the combustible material with oxygen. This fact he established beyond a doubt. On burning phosphorus in a jar of oxygen, he observed that a considerable quantity of the gas disappeared, that the phosphorus gained considerably in weight, and that the increase of the latter exactly corresponded to the loss of the former. An iron wire was burnt in a similar manner, and the weight of the oxidized iron was found equal to that of the wire originally employed, added to the quantity of oxygen which had disappeared. That the oxygen is really present in the oxidized body he proved by a very decisive experiment. Some liquid mercury was confined in a vessel of oxygen gas, and exposed to a temperature sufficient for causing its oxidation. The oxide of mercury, so produced, was put into a small retort and heated to redness, when it was reconverted into oxygen and fluid mercury, the quantity of the oxygen being exactly equal to what had combined with the mercury in the first part of the operation.

To account for the production of heat and light during combustion, Lavoisier had recourse to Dr Black's Theory of latent caloric. Heat is always evolved, whenever a substance, without change of form, passes from a rarer into a denser state, and also when a gas becomes liquid or solid, or a liquid solidifies; because a quantity of caloric previously combined, or latent within it, is then set free. Now this is precisely what happens in many instances of combustion. Thus water is formed by the burning of hydrogen, in which case two gases give rise to a liquid; and in forming phosphoric acid with phosphorus, or in oxidizing the metals, oxygen is condensed into a solid. When the product

of combustion is gaseous, as in the burning of charcoal, the evolution of heat is ascribed to the circumstance that the oxidized body contains a less quantity of combined caloric, or has a less specific caloric, than the substances which form it.

This is the weak point of Lavoisier's theory. Chemical action is very often accompanied by an increase of temperature, and the caloric evolved during combustion is only a particular instance of it. Any theory, therefore, by which it is proposed to account for the production of heat in some cases, ought to be applicable to all. When combustion, or any other chemical action is followed by a considerable condensation, in consequence of which the new body contains less insensible caloric than its elements did before combination, it is obvious that heat will, in that case, be disengaged. But if this is the sole cause of the phenomenon, it follows that a rise of temperature ought always to be preceded by a corresponding diminution of capacity for caloric, and that the extent of the former ought to be in a constant ratio with the degree of the latter. Now Petit and Dulong infer from their researches on this subject, (*Annales de Chim. et de Phys.* vol. x.) that the degree of heat developed during combination, bears no relation to the specific caloric of the combining substances; and that in the majority of cases, the evolution of heat is not attended by any diminution in the capacity of the compound. It is a well-known fact that an increase of temperature frequently attends chemical action, though the products contain much more insensible caloric than the substances which form them. This happens remarkably in the explosion of gun-powder, which is attended by an intense heat; and yet its materials, in passing from the solid to the gaseous state, expand at least to 250 times their volume, and consequently render latent a large quantity of caloric.

These circumstances leave no doubt that the evolution of caloric during chemical action is owing to some cause quite unconnected with that assigned by Lavoisier; and if this cause operates so powerfully in some cases, it is fair to infer that a part of the effect must be owing to it on those occasions, when the phenomena appear to depend on a change of capacity alone. A new theory is therefore required to account for the chemical production of heat. But it is easier to perceive the fallacies of one doctrine, than to substitute another which shall be faultless; and it appears to me that chemists must, for the present, be satisfied with the simple statement, that energetic chemical action does of itself give rise to an increase of temperature. Sir H. Davy and Berzelius, indeed, regard the heat of combination as an electrical phenomenon, on the supposition that the two combining substances are oppositely electrified. But such an opinion can hardly be maintained, except by those who assume that electricity is the cause of chemical affinity,—an opinion which I have not adopted for reasons already stated. Nor do we gain materially by the supposition; for the cause of production of heat, when two oppositely electrified bodies communicate with one another, is no less obscure and unintelligible than the phenomena which it is employed to explain.

## SECTION IV.

## HYDROGEN.

This gas was formerly termed *inflammable* air from its combustibility, and *phlogiston* from the supposition that it was the matter of heat; but the name *hydrogen*, derived from *ὕδωρ* *water*, has now become general. Its nature and leading properties were first pointed out by Mr Cavendish.

Hydrogen gas may be easily prepared in two ways. The first consists in passing the vapour of water over metallic iron heated to redness. This is done by putting iron wire into a gun-barrel open at both ends, to one of which is attached a retort containing pure water, and to the other a bent tube. The gun-barrel is placed in a furnace, and when it has acquired a full red heat, the water in the retort is made to boil briskly. The gas, which is copiously disengaged as soon as the steam comes in contact with the glowing iron, passes along the bent tube, and may be collected in convenient vessels, by dipping the free extremity of the tube into the water of a pneumatic trough\*. The second and most convenient method consists in putting pieces of iron or zinc into dilute sulphuric acid, formed of one part of strong acid to four or five of water. Zinc is generally preferred. The hydrogen obtained in these processes is not absolutely pure. The purest iron wire contains traces of charcoal, in consequence of which the gas, formed by its means, is apt to contain carbonic acid, and most probably carburetted hydrogen. The zinc of commerce contains both charcoal and sulphur, so that in addition to the gases just mentioned, the hydrogen derived from this source is contaminated with sulphuretted, and perhaps with carburetted hydrogen. A little metallic zinc is also contained in it, apparently in combination with hydrogen. All these impurities, carburetted hydrogen excepted, may be removed by passing the hydrogen through a solution of pure potash. To obtain hydrogen of great purity, distilled zinc should be employed.

Hydrogen is a colourless gas, and has neither odour nor taste when perfectly pure. It is a powerful refractor of light. Like oxygen, it cannot be resolved into more simple parts, and, like that gas, has hitherto resisted all attempts to compress it into a liquid. It is the lightest body in nature, and is consequently the best material for filling balloons. It is exactly 16 times lighter than oxygen, and therefore 100 cubic inches of it at 60° F. and 30 Bar. must weigh  $\frac{33.888}{16}$

or 2.118 grains. Its specific gravity is consequently 0.0694, as stated some years ago by Dr Prout.

Hydrogen does not change the blue colour of vegetables. It is sparingly absorbed by water, 100 cubic inches of that liquid dissolving about one and a half of the gas. It cannot support respiration; for an animal soon perishes when confined in it. Death ensues from deprivation of oxygen rather than from any noxious quality of the hydrogen, since an atmosphere composed of a due proportion of oxygen and hydrogen may be respired without inconvenience. Nor is it a supporter

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\* The mode of collecting gases, together with the apparatus employed for that purpose, will be described in the fourth part of this work.

of combustion ; for when a lighted candle fixed on wire is passed up into an inverted jar full of hydrogen, the light disappears on the instant.

Hydrogen gas is inflammable in an eminent degree, though, like other combustibles, it requires the aid of a supporter for enabling its combustion to take place. This is exemplified by the experiment above alluded to, in which the gas is kindled by the flame of the candle, but burns only where it is in contact with the air. Its combustion, when conducted in this manner, goes on tranquilly, and is attended with a yellowish blue flame and a very feeble light. The phenomena are different when the hydrogen is previously mixed with a due quantity of atmospheric air. The approach of flame not only sets fire to the gas near it, but the whole is kindled at the same instant ; a flash of light passes through the mixture, which is followed by a violent explosion. The best proportion for the experiment is two measures of hydrogen, to five or six of air. The explosion is far more violent when pure oxygen is used instead of atmospheric air, particularly when the gases are mixed together in the ratio of one measure of oxygen to two of hydrogen.

Oxygen and hydrogen gases cannot combine at ordinary temperatures, and may, therefore, be kept in a state of mixture without even gradual combination taking place between them. Hydrogen may be set on fire, when in contact with air or oxygen gas, by flame, by a solid body heated to bright redness, and by the electric spark. If a jet of hydrogen be thrown upon recently prepared spongy platinum, this metal almost instantly becomes red-hot, and then sets fire to the gas, a discovery which was made three years ago by Professor Doebereiner of Jena. The power of flame and electricity in causing a mixture of hydrogen with an air or oxygen gas to explode, is limited. Mr Cavendish found that flame occasions a very feeble explosion when the hydrogen is mixed with nine times its bulk of air ; and that a mixture of four measures of hydrogen to one of air does not explode at all. An explosive mixture formed of two measures of hydrogen to one of oxygen, explodes from all the causes above enumerated. M. Biot found that sudden and violent compression likewise causes an explosion, apparently from the heat emitted during the operation ; for an equal degree of condensation, slowly produced, has not the same effect. The electric spark ceases to cause a detonation when the explosive mixture is diluted with twelve times its volume of air, fourteen of oxygen, or nine of hydrogen, or when it is expanded to sixteen times its bulk by diminished pressure. I find that spongy platinum acts just as rapidly as flame or the electric spark in producing an explosion, provided the gases are quite pure and mixed in the exact ratio of two to one\*.

When the action of heat, the electric spark, and spongy platinum no longer cause an explosion, a silent and gradual combination between the gases may still be occasioned by them. Sir H. Davy observed that oxygen and hydrogen unite slowly with one another, when they

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\* For a variety of facts respecting the causes which prevent the action of flame, electricity, and platinum in producing an explosion, the reader may consult the Essay of M. Grotthus in the *Ann. de Chimie*, v. lxxxii. Sir H. Davy's work on Flame ; Dr Henry's Essay in the *Philosophical Transactions* for 1824 ; and a paper by myself in the *Edinburgh Philosophical Journal* for the same year.

are exposed to a temperature above the boiling point of mercury, and below that at which glass begins to appear luminous in the dark. An explosive mixture diluted with air to too great a degree to explode by electricity, is made to unite silently by a succession of electric sparks. Spongy platinum causes them to unite slowly, though mixed with one hundred times their bulk of oxygen gas.

A large quantity of caloric is evolved during the combustion of hydrogen gas. Lavoisier concludes from experiments made with his calorimeter, (*Elements*, vol. i.) that one pound of hydrogen occasions so much heat in burning as is sufficient to melt 295.6 pounds of ice. Mr Dalton fixes the quantity of ice at 320 pounds, and Dr Crawford at 480. The most intense heat that can be produced, is caused by the combustion of hydrogen in oxygen gas. Dr Hare of Philadelphia, who first burned hydrogen for this purpose, collected the gases in separate gas-holders, from which a stream was made to issue through tubes communicating with one another, just before their termination. At this point the jet of the mixed gases was inflamed. The effect of the combustion, though very great, is materially increased by forcing a proper mixture of the two gases into a strong metallic syringe, and burning them as they escape from it. An apparatus of this kind, now known by the name of the oxy-hydrogen blowpipe, was contrived by Mr Newman, and was employed by the late Professor Clarke in his experiments on the fusion of refractory substances. On opening a stopcock which confines the condensed gases, a jet of the explosive mixture issues with force through a small blowpipe tube, at the extremity of which it is kindled. In this state, however, the apparatus should never be used; for, as the reservoir is itself full of an explosive mixture, there is great danger of the flame running back along the tube and setting fire to the whole gas at once. To prevent the occurrence of such an accident, which would most probably prove fatal to the operator, Professor Cumming proposed that the gas, as it issues from the reservoir, should be made to pass through a cylinder full of oil or water before reaching the point at which it is to burn; and Dr Wollaston suggested the additional precaution of fixing successive layers of fine wire gauze within the exit tube, each of which should intercept the communication of flame. But this apparatus is rarely necessary in chemical researches. A very intense heat, quite sufficient for most purposes, may be safely and easily procured by passing a jet of oxygen gas through the flame of a spirit lamp, as proposed by the late Dr Marcet.

Water is the sole product of the combustion of hydrogen gas. For this important fact, we are indebted to Mr Cavendish. He demonstrated it by burning oxygen and hydrogen gases in a dry glass vessel, when a quantity of pure water was generated exactly equal in weight to that of the gases which had disappeared. This experiment, which is the synthetic proof of the composition of water, was afterwards made on a much larger scale in Paris, by Vauquelin, Fourcroy, and Seguin. Lavoisier first demonstrated its nature analytically, by passing a known quantity of watery vapour over metallic iron heated to redness in a glass tube. Hydrogen gas was disengaged, the metal in the tube was oxidized, and the weight of the former, added to the increase which the iron had experienced from combining with oxygen, exactly corresponded to the quantity of water which had been decomposed.

It will soon appear that a knowledge of the exact proportions in



which oxygen and hydrogen gases unite to form water is a necessary element in many chemical reasonings. Its composition by volume was demonstrated very satisfactorily by Messrs Nicholson and Carlisle, in their researches on the chemical agency of galvanism. On resolving water into its elements by this agent, and collecting them in separate vessels, they obtained precisely two measures of hydrogen to one of oxygen,—a result which has been fully confirmed by subsequent experimenters. The same fact was proved synthetically by Gay-Lussac and Humboldt, in their Essay on Eudiometry, published in the *Journal de Physique* for 1805. They found that when a mixture of oxygen and hydrogen is inflamed by the electric spark, those gases always unite in the exact ratio of one to two, whatever may be their relative quantity in the mixture. When one measure of oxygen is mixed with three of hydrogen, one measure of hydrogen is the residue after the explosion; and a mixture of two measures of oxygen and two of hydrogen leaves one measure of oxygen. When one volume of oxygen is mixed with two of hydrogen, both gases, if quite pure, disappear entirely on the electric spark being passed through them. The composition of water by weight was determined with great care by Berzelius and Dulong; and we cannot hesitate, considering the known dexterity of the operators, and the principle on which their method of analysis was founded, to regard their result as a nearer approximation to the truth than that of any of their predecessors. They state as a mean of three careful experiments, (*Ann. de Ch. et de Ph.* vol. xv.) that 100 parts of pure water consist of 88.9 of oxygen and 11.1 of hydrogen. Now,

$$11.1 : 88.9 :: 1 : 8.009$$

which is so near the proportion of 1 to 8 as to justify the adoption of that ratio. Hence, the constitution of water by weight and measure, may be thus stated:

	By Weight.	By Volume.
Oxygen .	8	1
Hydrogen .	1	2

These are the data from which it was inferred that oxygen gas is just 16 times heavier than hydrogen. The atomic weights of oxygen and hydrogen are deduced from the same analysis. As no compound of these substances is known which has a less proportion of oxygen than water, it is supposed to contain one atom of each of its constituents. This view of the atomic constitution of water is justified by the strong affinity which its elements evince for one another, as well as from the proportions with which they respectively combine with other bodies. The reasons for rejecting the idea of its being formed of one atom of oxygen to two atoms of hydrogen have been already stated. Consequently, regarding the atom of hydrogen as unity, eight will be the relative weight of an atom of oxygen.

The processes for forming hydrogen gas will now be intelligible. The first is the method by which Lavoisier made the analysis of water. It is founded on the fact that iron at a red heat decomposes water, the oxygen of that liquid uniting with the metal, and hydrogen gas being set free. That the hydrogen which is evolved when zinc or iron is put into dilute sulphuric acid must be derived from the same source, is obvious from the consideration that of the three substances, iron, sulphuric acid, and water, the last is the only one which contains hydro-

gen. The product of the operation, besides hydrogen, is the sulphate of the protoxide of iron, if iron is used, or of the oxide of zinc, when zinc is employed. The knowledge of the combining proportions of these substances will readily give the exact quantity of each product. These numbers are,

Water (8 oxy. + 1 hyd.)	9
Sulphuric acid	40
Iron	28
Protoxide of iron (28 iron + 8 oxygen)	36
Sulphate of the protoxide of iron (40 + 36)	76

Hence for every 9 grains of water which is decomposed, 1 grain of hydrogen will be set free; 8 grains of oxygen will unite with 28 grains of iron, forming 36 of the protoxide of iron; and the 36 grains of the protoxide will combine with 40 grains of sulphuric acid, forming 76 of the sulphate of the protoxide of iron. A similar calculation may be employed when zinc is used, merely by substituting the atomic weight of zinc (34) for that of iron.—According to Mr Cavendish, an ounce of zinc yields 676 cubic inches, and an equal quantity of iron 782 cubic inches of hydrogen gas.

The action of diluted sulphuric acid on metallic zinc affords an instance of what was once called Disposing Affinity. Zinc cannot decompose water at common temperatures; but as soon as sulphuric acid is added, the decomposition of the water takes place rapidly, though the acid merely unites with the oxide of zinc. The former explanation was, that the affinity of the acid for the oxide of zinc disposed the metal to unite with the oxygen, and thus enabled it to decompose water; that is, the oxide of zinc was supposed to produce an effect previous to its existence. The obscurity of this explanation arises from regarding changes as consecutive, which are in reality simultaneous. There is no appearance of succession in the process; the oxide of zinc is not formed previously to its combination with the acid, but at the same instant. There is, as it were, only one chemical change, which consists in the combination at one and the same moment of the zinc with the oxygen, and the oxide of zinc with the acid; and this change occurs because these two affinities, acting together, overcome the attraction of oxygen and hydrogen for one another.

Water is a transparent colourless liquid, which has neither smell nor taste. It is a powerful refractor of light, conducts heat very slowly, and is an imperfect conductor of electricity. It is compressible by very strong pressure. This fact was long disputed; but Mr Perkins finds that the pressure of 2000 atmospheres occasions a diminution of 1-12th of its bulk. The relations of water, with respect to caloric, are highly important, but have already been discussed in the first part of the work. The specific gravity of water is 1, the density of all solid and liquid bodies being referred to it as a term of comparison. One cubic inch at 60° F. and 30 Bar., weighs 252.525 grains, so that it is 828 times heavier than atmospheric air.

Water is one of the most powerful chemical agents which we possess. Its agency is owing partly to the extensive range of its own affinity, and partly to the nature of its elements. The effect of the last circumstance has already appeared in the formation of hydrogen gas; and indeed there are few complex chemical changes which do not give rise either to the production or decomposition of water. But, independently of the elements of which it is composed, it combines directly with many

bodies. Sometimes it is contained in a variable ratio, as in ordinary solution; in other compounds it is present in a fixed definite proportion, as is exemplified by its union with several of the acids, the alkalis, and all sorts that contain water of crystallization. These combinations are termed *hydrates*; thus, the strongest liquid sulphuric acid is a compound of one atom of the real dry acid and one atom of water; and its proper name is *hydrous sulphuric acid*, or *hydrate of sulphuric acid*. The adjunct *hydro* has been sometimes used to signify the presence of water in definite proportion; but it is advisable, to prevent mistakes, to limit its employment to the compounds of hydrogen.

The purest water which can be found as a natural product, is procured by melting freshly fallen snow, or by receiving rain in clean vessels at a distance from houses. But this water is not absolutely pure; for if placed under the exhausted receiver of an air pump, or boiled briskly for a few minutes, bubbles of gas escape from it. The air obtained in this way from snow water, is much richer in oxygen gas than atmospheric air. According to the experiments of Gay-Lussac and Humboldt, it contains 34.8 per cent. of oxygen, and the air separated by ebullition from rain-water contains 32 per cent. of that gas. All water which has once fallen on the ground, becomes impregnated with more or less earthy or saline matters, and it can be separated from them only by distillation. The distilled water, thus obtained, and preserved in clean well-stopped bottles, is absolutely pure. Recently boiled water has the property of absorbing a portion of all gases, when its surface is in contact with them; and the absorption is promoted by brisk agitation. The following table, from Dr Henry's Chemistry, shows the absorbability of different gases by water, deprived of all its air by ebullition.

100 cubic inches of such water, at the mean temperature and pressure, absorb of

	Dalton and Henry.	Saussure.
Sulphuretted Hydrogen	100 C. J.	253
Carbonic Acid	100	106
Nitrous Oxide	100	76
Olefiant Gas	12.5	15.3
Oxygen	3.7	6.5
Carbonic Oxide	1.56	6.2
Nitrogen	1.56	4.1
Hydrogen	1.56	4.6

The estimate of Saussure is in general too high. That of Mr Dalton and Dr Henry for nitrous oxide is considerably beyond the truth, according to the experiments of Sir H. Davy.

### *Deutoxide of Hydrogen.*

The deutoxide, or peroxide of hydrogen, was discovered by M. Thénard in the year 1818. Before describing the mode of preparing this compound, it must be observed that there are two oxides of barium, and that when the peroxide of that metal is put into water containing free muriatic acid, oxygen gas is set at liberty, and the peroxide is converted into the protoxide of barium or baryta, which combines with the acid. When this process is conducted with the necessary precautions, the oxygen which is set free, instead of escaping in the form of gas, unites with the hydrogen of the water, and brings it to.

maximum of oxidation. For a full detail of all the minutiae of the process, the reader may consult the original memoir of M. Thénard\*; the general directions are the following:—To six or seven ounces of water, add so much pure concentrated muriatic acid as is sufficient to dissolve 230 grains of baryta, and after having placed the mixed fluids in a glass vessel surrounded with ice, add in successive portions 185 grains of the deutoxide of barium reduced to powder, and stir with a glass rod after each addition. When the solution, which takes place without effervescence, is complete, sulphuric acid is added in sufficient quantity for precipitating the whole of the baryta in the form of an insoluble sulphate, so that the muriatic acid which had been combined with that earth, is completely separated from it. Another portion of the deutoxide of barium, amounting to 185 grains, is then put into the liquid; the free muriatic acid instantly acts upon it, and as soon as it is dissolved, the baryta is again converted into a sulphate by the addition of sulphuric acid. The solution is then filtered, to separate the insoluble sulphate of baryta, and fresh quantities of the peroxide of barium are added in succession, till about three ounces of it have been employed. The liquid then contains from 25 to 30 times its volume of oxygen gas. The muriatic acid which has served to decompose the peroxide of barium during the whole process, is now removed by the cautious addition of the sulphate of silver, and the sulphuric acid is afterwards separated by solid baryta.

The peroxide of hydrogen, as thus prepared, is still diluted with a considerable quantity of water. To separate the latter, the mixed liquids are placed under the exhausted receiver of an air pump, with a vessel of strong sulphuric acid. As the water evaporates, the density of the residue increases, till at last it acquires the specific gravity of 1.452. The concentration cannot be pushed farther; for if kept under the receiver after reaching this point, the peroxide itself gradually but slowly volatilizes without change.

The peroxide of hydrogen of sp. gr. 1.452 is a colourless transparent liquid without odour. It whitens the surface of the skin when applied to it, causes a prickling sensation, and even destroys its texture if the application is long continued. It acts in a similar manner on the tongue, in addition to which it thickens the saliva, and tastes like certain metallic solutions. Brought into contact with litmus and turmeric paper, it gradually destroys their colour and makes them white. It is slowly volatilized in vacuo, which shows that its vapour is much less elastic than that of water. It preserves its liquid form at all degrees of cold to which it has hitherto been exposed. At the temperature of 59° F. it is decomposed, being converted into water and oxygen gas. For this reason it ought to be preserved in glass tubes surrounded with ice.

The most remarkable property of the peroxide of hydrogen is the facility with which it is decomposed. The diffused day-light does not seem to exert any influence over it, and even the direct solar rays act upon it tardily. It effervesces from the escape of oxygen at 59° F., and the sudden application of a higher temperature, as of 212° F., gives rise to such a rapid evolution of gas as to cause an explosion. Water, apparently by combining with the peroxide, renders it more

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\* In the An. de Chim. et de Phys. vol. viii. ix. and x.; Annals of Philosophy, vol. xiii. and xiv.; and M. Thénard's *Traité de Chimie*.

permanent ; but no degree of dilution can enable it to bear the heat of boiling water, at which temperature it is decomposed entirely. All the metals except iron, tin, antimony, and tellurium, have a tendency to decompose the peroxide of hydrogen, converting it into oxygen and water. A state of minute mechanical division is essential for producing rapid decomposition. If the metal is in mass, and the peroxide diluted with water, the action is slow. The metals which have a strong affinity for oxygen are oxidized at the same time, such as potassium, sodium, arsenic, molybdenum, manganese, zinc, tungsten, and chromium ; while others, such as gold, silver, platinum, iridium, osmium, rhodium, palladium, and mercury, retain the metallic state.

The peroxide of hydrogen is decomposed at common temperatures by many of the metallic oxides. That some of the protoxides should have this effect, would be anticipated in consequence of their tendency to pass into a higher state of oxidation. The protoxides of iron, manganese, tin, cobalt, and others, act on this principle, and are really converted into peroxides. The peroxides of barium, strontium and calcium may likewise be formed by the action of the peroxide of hydrogen on baryta, strontia, and lime. But it is a singular fact, and I am not aware that any satisfactory explanation of it has been given, that some oxides decompose the peroxide of hydrogen without passing into a higher degree of oxidation. The peroxides of silver, lead, mercury, gold, platinum, manganese, and cobalt, possess this property in the greatest perfection, acting on the peroxide of hydrogen, when concentrated, with surprising energy. The decomposition is complete and instantaneous ; oxygen gas is evolved so rapidly as to produce a kind of explosion, and such an intense temperature is excited, that the glass tube in which the experiment is conducted becomes red-hot. The reaction is very great even when the peroxide of hydrogen is diluted with water. The oxide of silver occasions a very perceptible effervescence when put into water which contains only 1-50th its bulk of oxygen. All the metallic oxides, which are decomposed by a red heat, such as those of gold, platinum, silver, and mercury, are reduced to the metallic state when they act upon the peroxide of hydrogen. This effect cannot be altogether ascribed to the caloric disengaged during the action ; for the oxide of silver suffers reduction when put into a very dilute solution of the peroxide, although the decomposition is not then attended by an appreciable rise of temperature.

While the tendency of metals and metallic oxides is to decompose the peroxide of hydrogen, acids have the property of rendering it more stable. In proof of this, let a portion of that liquid, somewhat diluted with water, be heated till it begins to effervesce from the escape of oxygen gas ; let some strong acid, as the nitric, sulphuric, or muriatic, be then dropped into it, and the effervescence will cease on the instant. When a little gold in a state of fine division is put into a weak solution of the peroxide of hydrogen, containing only 10, 20, or 30 times its bulk of oxygen, a brisk effervescence ensues ; but on letting one drop of sulphuric acid fall into it, the effervescence ceases instantly ; it is reproduced by the addition of potash, and is again arrested by adding a second portion of acid. The only acids that do not possess this property are those that have a low degree of acidity, as the carbonic and boracic acids ; or those which suffer a chemical change when mixed with the peroxide of hydrogen, as the hydriodic and sulphurous acids, and sulphuretted hydrogen. Acids appear to increase the sta-



bility of the peroxide in the same way as water does, namely, by combining chemically with it. Several compounds of this kind were formed by Thénard, before he was aware of the existence of the peroxide of hydrogen. They were made by dissolving the peroxide of barium in some diluted acid, such as the nitric, and then precipitating the baryta by sulphuric acid. As the nitric acid was supposed under these circumstances to combine with an additional quantity of oxygen, Thénard applied the term oxygenized nitric acid to the resulting compound, and described several other new acids under a similar title. But the subsequent discovery of the peroxide of hydrogen put the nature of the oxygenized acids in a clearer light; for their properties are easily explicable on the supposition that they are composed, not of acids and oxygen gas, but of acids united with the peroxide of hydrogen.

The peroxide of hydrogen was analyzed by diluting a known weight of it with water, and then decomposing it by boiling the solution. According to two careful analyses, conducted on this principle, 864 parts of the peroxide of hydrogen are composed of 466 of water, and 398 of oxygen gas. The 466 of water contain 414 of oxygen, whence it may be inferred that the peroxide of hydrogen contains twice as much oxygen as water. A small deficiency of oxygen in the experiment was to be expected, owing to the difficulty of obtaining the peroxide of hydrogen perfectly free from water. The peroxide consists, therefore, of

Hydrogen	1	1 proportion.
Oxygen	16	2 proportions.

## SECTION V.

### NITROGEN.

The existence of nitrogen gas, as distinct from every other gaseous substance, appears to have been first noticed by the late Dr Rutherford, in 1772. Lavoisier discovered that it is a constituent part of the atmosphere in 1775, and the same discovery was made soon after, or about the same time, by Scheele. Lavoisier called it Azote, from *a privative*, and *ζωή* life, because it is unable to support the respiration of animals; but as it possesses this negative property in common with most other gases, the more appropriate term nitrogen has been since applied to it, from the circumstance of its being an essential ingredient of nitric acid.

Nitrogen is most conveniently prepared by burning a piece of phosphorus in a jar full of air inverted over water. The strong affinity of phosphorus for oxygen enables it to burn till the whole of that gas is consumed. The product of the combustion, phosphoric acid, is at first diffused through the residue in the form of a white cloud; but as this substance is rapidly absorbed by water, it disappears entirely in the course of half an hour. The residual gas is nitrogen, containing a small quantity of carbonic acid and vapour of phosphorus, both of which may be removed by agitating it briskly with a solution of pure potash. Several other substances may be employed for withdrawing

the oxygen from atmospheric air. A solution of the proto-sulphate of iron, charged with the deutoxide of nitrogen, absorbs the oxygen in the space of a few minutes. A stick of phosphorus produces the same effect in 24 hours, if exposed to a temperature of 60° F. A solution of the sulphuret of potash or of lime acts in a similar manner; and a mixture of equal parts of iron filings and sulphur, made into a paste with water, may be employed with the same intention. Both these processes, however, are inconvenient from their slowness. Nitrogen gas may likewise be obtained by exposing a mixture of fresh muscle and nitric acid of specific gravity 1.20 to a moderate temperature. A large quantity of gaseous matter is evolved with effervescence, which is nitrogen mixed with a little carbonic acid. The latter must be removed by agitation with lime water; but the residue still retains a peculiar odour, indicative of the presence of some volatile principle which cannot be wholly separated from it. The theory of this process is somewhat complex, and will be considered more conveniently in a subsequent section.

Pure nitrogen is a colourless gas, wholly devoid of smell and taste. It does not change the blue colour of vegetables, and is distinguished from other gases more by negative characters than any striking quality. It is not a supporter of combustion; but, on the contrary, extinguishes all burning bodies that are immersed in it. No animal can live in it; but yet it exerts no injurious action either on the lungs or on the system at large, the privation of oxygen gas being the sole cause of death. It is not inflammable like hydrogen, though, under favourable circumstances, it may be made to unite with oxygen. Water, when deprived of air by ebullition, takes up about one and a half per cent. of it. Its specific gravity is 0.9722\*; and, therefore, 100 cubic inches of it at the mean temperature and pressure, will weigh 29.652 grains.

Considerable doubt exists as to the nature of nitrogen. Though ranked among the simple non-metallic bodies, some circumstances have led to the suspicion that it is compound, and this opinion has been warmly advocated by Sir H. Davy and Berzelius. The chief argument in favour of this view is drawn from the phenomena that attend the formation of what is called the *ammoniacal amalgam*. From the metallic appearance of this substance, it was supposed to be a compound of mercury and a metal; and as the only method of forming it is by the action of galvanism on a salt of ammonia, in contact with a globule of mercury, it follows that the metal, if present at all, must have been supplied by the ammonia. Now ammonia is composed of hydrogen and nitrogen; and as the former, from its levity, could hardly be supposed to contain a metal, it was inferred that it must be present in the latter. Unfortunately for this argument, the metal cannot be obtained in a separate state. The amalgam no sooner ceases to be under the galvanic influence than its elements begin to separate spontaneously, and in a few minutes the decomposition is complete, the sole products being ammonia, hydrogen, and pure mercury. Sir H. Davy accounts for this change on the supposition that water is decomposed; that its oxygen reproduces nitrogen by uniting with the

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\* This number is calculated on the assumption that air consists of one measure of oxygen to four of nitrogen, and that 1.1111 is the specific gravity of oxygen gas. See Thomson's *First Principles*, vol. i. p. 99.

supposed metal ; and that one part of its hydrogen forms ammonia by uniting with the nitrogen, while the remainder escapes in the form of gas. But Gay-Lussac and Thénard, (*Recherches Physico-Chimiques*, vol. i.) declare that the amalgam resolves itself into mercury, ammonia, and hydrogen, even though perfectly free from moisture ; and infer from their experiments that it is composed of those three substances combined directly with one another. It hence appears that the examination of the ammoniacal amalgam affords no proof of the compound nature of nitrogen ; nor was Sir H. Davy's attempt to decompose that gas by aid of potassium, intensely heated by a galvanic current, attended with better success. Berzelius has defended the idea that nitrogen is a compound body on other principles ; but as his arguments, though very ingenious, are merely speculative, they cannot be admitted as decisive of the question.

### *On the Atmosphere.*

The earth is every where surrounded by a mass of gaseous matter called the atmosphere, which is preserved at its surface by the force of gravity, and revolves together with it around the sun. It is colourless and invisible ; excites neither taste nor smell when pure, and is not sensible to the touch unless when it is in motion. It possesses the physical properties of elastic fluids in a high degree. The knowledge of its exact weight is an essential element in many physical and chemical researches, and has therefore been determined with much care. According to the experiments of Sir G. Shuckburgh Evelyn, 100 cubic inches of pure and dry atmospheric air at 60° F. and 30 Bar., weigh exactly 30.5 grains. Its specific gravity is unity, being the standard with which the density of all other elastic fluids is compared. Its pressure at the level of the sea is equal to a weight of about 15 pounds on every square inch of surface, and can support a column of water 34 feet high, and a column of mercury of 30 inches. It may be diminished in volume to a great extent by compression ; and it appears from some recent experiments of Mr Perkins that it becomes liquid under a pressure of 2000 atmospheres. This requires confirmation : if true, it is probable that pure oxygen and nitrogen gases may also be liquefied by the same degree of compression.

The extreme compressibility and elasticity of the air accounts for the facility with which it is set in motion, and the velocity with which it is capable of moving. It is subject to the laws which characterize elastic fluids in general. It presses, therefore, equally on every side ; and when some parts of it become lighter than the surrounding portions, the denser particles rush rapidly into their place and force the more rarefied ones to ascend. The motion of air gives rise to various familiar phenomena. A stream or current of air is wind, and an undulatory vibration excites the sensation of sound.

The atmosphere is not of equal density at all its parts. This is obvious from the consideration that those portions of it which are next the earth sustain the whole pressure of the atmosphere, while the higher strata bear only a part of it. The atmospheric column diminishes in length as the distance from the earth's surface increases ; and, consequently, the greater the elevation, the lighter must be the air. It is not known to what height the atmosphere extends. From calculations founded on the phenomena of refraction, its height is supposed to be about 45 miles ; and Dr Wollaston estimates, from the law of ex-

pansion of gases, that it is 40 miles. How far it extends beyond this point is a subject for speculation. If matter is infinitely divisible, as many philosophers have supposed, there ought to be no limit to the extent of the atmosphere; it should, on that supposition, pervade all space, and accumulate about the sun, moon, and planets, forming around each an atmosphere, the density of which should depend on their respective forces of attraction. But Dr Wollaston infers from astronomical observations made by himself and Captain Kater, that there is no solar atmosphere; and the observations of other astronomers appear to justify the same conclusion with respect to the planet Jupiter. The extent of the atmosphere must therefore be limited. Now the only mode of accounting for the finite extent of the atmosphere, is on the supposition that the air is composed of indivisible particles or atoms; and if this be true of one kind of matter, there can be no doubt that material substances, in general, are of a similar nature. Consequently, the absence of an atmosphere around the sun and planets demonstrates the truth of the atomic theory\*.

Air was one of the four elements of the ancient philosophers, and their opinion of its nature prevailed generally till its accuracy was rendered questionable by the experiments of Boyle, Hooke, and Mayow. The discovery of oxygen gas in 1774 paved the way to the knowledge of its real composition, which was discovered about the same time by Scheele and Lavoisier. The former exposed some atmospheric air to a solution of the sulphuret of potash, which gradually absorbed the whole of the oxygen. Lavoisier effected the same object by the combustion of iron-wire and phosphorus.

The earlier analyses of the air did not agree very well with one another. According to the researches of Lavoisier, it is composed of 27 measures of oxygen to 73 of nitrogen. The analysis of Scheele gave a somewhat higher proportion of oxygen. Priestley found that the quantity of oxygen varies from 20 to 25 per cent.; and Cavendish estimated it only at 20. These discrepancies must have arisen from imperfections in the mode of analysis; for the proportion of oxygen has been found by subsequent experiments to be almost, if not exactly, that which was stated by Mr Cavendish. The results of Scheele and Priestley are clearly referrible to this cause. It is now known that the processes they employed cannot be relied on, unless certain precautions are taken of which those chemists were ignorant. Recently boiled water absorbs nitrogen; and, consequently, if the sulphuret of potash be dissolved in that liquid by the aid of heat, the solution takes up a portion of nitrogen during the process, and thereby renders the apparent absorption of oxygen too great. This inconvenience may be avoided by dissolving the alkaline sulphuret in cold unboiled water. The deutoxide of nitrogen, employed by Priestley, removes all the oxygen in the course of a few seconds; but for reasons which will soon be mentioned, its indications are very apt to be fallacious. The combustion of phosphorus, as well as the gradual oxidation of that substance, acts in a very uniform manner, and removes the whole of the oxygen completely. The residual nitrogen contains a little of the vapour of phosphorus, which increases the bulk of that gas by 1-40th,

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\* See Dr Wollaston's paper on the Finite Extent of the Atmosphere in the Phil. Trans. for 1822.

for which an allowance must be made in estimating the real quantity of nitrogen.

Since chemists have learned the precautions to be taken in the analysis of the air, a close correspondence has been observed in the results of their experiments upon it. The researches of Davy, Dalton, Gay-Lussac, Thomson, and others, leave no doubt that 100 measures of pure atmospheric air consist of 20 or 21 volumes of oxygen, and 80 or 79 of nitrogen. Dr Thomson, whose analysis is the most recent, fixes the quantity of oxygen at 20 per cent., and the reasons he has assigned for regarding this estimate as more accurate than the other, appear satisfactory. The oxygen was determined (First Principles of Chemistry, vol. i. p. 97,) by mixing with the air a quantity of hydrogen, sufficient to convert all the oxygen present into water, and kindling the mixture by the electric spark. Water is formed and is condensed; and since that liquid is composed of one volume of oxygen to two of hydrogen, one-third of the diminution must give the exact quantity of oxygen. This process is so easy of execution, and so uniform in its indications, that it is now employed nearly to the total exclusion of all others.

Such is the constitution of pure atmospheric air. But the atmosphere is never absolutely pure; for it always contains a certain variable quantity of carbonic acid and watery vapour, besides the odorous matter of flowers and other volatile substances, which are also frequently present. The carbonic acid never exceeds one in 100 parts, provided there is a free circulation of air, and generally amounts only to 1-1000th or 1-2000th of the whole. Saussure found it in air collected at the top of Mont-Blanc; and, indeed, it exists at all altitudes which have been hitherto attained.

The chief chemical properties of the atmosphere are owing to the presence of oxygen gas. Air from which this principle has been withdrawn is nearly inert. It can no longer support respiration and combustion, and metals are not oxidized by being heated in it. Most of the spontaneous changes which mineral and dead organized matters undergo, are owing to the powerful affinities of oxygen. The uses of nitrogen are in a great measure unknown. It was supposed to act as a mere diluent to the oxygen; but it most probably serves some useful purpose in the economy of animals, the exact nature of which has not been discovered.

The knowledge of the composition of the air, and of the importance of oxygen to the life of animals, naturally gave rise to the notion that the healthiness of the air, at different times and in different places, depends on the relative quantity of this gas. It was therefore supposed that the purity of the atmosphere, or its fitness for communicating health and vigour, might be discovered by determining the proportion of oxygen; and hence the origin of the term *Eudiometer*, which was applied to the apparatus for analyzing the air. But this opinion, though at first supported by the discrepant results of the earlier analysts, was soon proved to be fallacious. It appears, on the contrary, that the composition of the air is not only constant in the same place, but is the same in all regions of the earth, and at all altitudes. Air collected at the summit of the highest mountains, such as Mont-Blanc and Chimborazo, contains the same proportion of oxygen as that of the lowest valleys. The air of Egypt was found by Berthollet to be similar to that of France. The air which Gay-Lussac brought from an altitude of 21,735 feet above the earth, had the same composition



as that collected at a short distance from its surface. Even the miasmata of marshes, and the effluvia of infected places, owe their noxious qualities to some principle of too subtle a nature to be detected by chemical means, and not to a deficiency of oxygen. Seguin examined the infectious atmosphere of a hospital, the odour of which was almost intolerable, and could discover no appreciable deficiency of oxygen, or other peculiarity of composition.

The question has been much discussed whether the oxygen and nitrogen gases of the atmosphere are simply mixed, or chemically combined with one another. Appearances are at first view greatly in favour of the latter opinion. Oxygen and nitrogen gases differ in density, and therefore it might be expected, were they merely mixed together, that the oxygen as the heavier gas, ought, in obedience to the force of gravity, to collect in the lower regions of the air, while the nitrogen should have a tendency to occupy the higher. But this has nowhere been observed. If air be confined in a long tube, preserved at perfect rest, the upper part of it will contain just as much oxygen as the lower, even after an interval of many months; nay, if the lower part of it be filled with oxygen, and the upper part with nitrogen, they will be found in the course of a few hours to have mixed intimately with one another. The constituents of the air are, also, in the exact proportion for combining. By measure they are in the simple ratio of one to four, which agrees perfectly with the law of combination by volume; by weight they are as 8 to 28, which is one proportion of oxygen to two of nitrogen.

Strong as are these arguments in favour of the chemical theory, it is nevertheless liable to objections which appear insuperable. The atmosphere possesses all the characters that should arise from a mechanical mixture. There is not, as in all other cases of chemical union, any change in the bulk, form, or other qualities of its elements. The nitrogen manifests no attraction for the oxygen. All bodies which have an affinity for oxygen, abstract it from the atmosphere with as much facility as if the nitrogen was absent altogether. Even water effects this separation; for the air which is expelled from rain water by ebullition, contains more than 20 per cent. of oxygen. When oxygen and nitrogen gases are mixed together in the ratio of 1 to 4, the mixture occupies precisely five volumes, and has every property of pure atmospheric air. The refractive power of the atmosphere is precisely such as a mixture of oxygen and nitrogen ought to have, and different from what would be expected were its elements chemically united. (Edinburgh Journal of Science, No. 8.)

Since the elements of the air cannot be regarded as in a state of actual combination, it is necessary to account for the steadiness of their proportion on some other principle. Chemists are divided on this subject between two opinions. It is conceived, according to one view, that the affinity of oxygen and nitrogen for one another, though insufficient to cause their combination when mixed together at ordinary temperatures, might still operate in such a manner as to prevent their separation; that a certain degree of attraction is even then exerted between them, which is able to counteract the tendency of gravity. An opinion of this kind was advanced by Berthollet, in his *Statique Chimique*, and was defended by the late Dr Murray. This doctrine, however, is not satisfactory. It is, indeed, quite conceivable that oxygen and nitrogen may attract each other in the way supposed; and it may be admitted that this supposition explains why these two

gases continue in a state of perfect mixture. But still the explanation is unsatisfactory; and for the following reason;—Mr Dalton took two cylindrical vessels, one of which was filled with carbonic acid, the other with hydrogen; the latter was placed perpendicularly over the other, and a communication was established between them. In the course of a few hours hydrogen was detected in the lower vessel, and carbonic acid in the upper. If the upper vessel be filled with oxygen, nitrogen, or any other gas, the same phenomena will ensue; the gases will be found, after a short interval, to be in a state of mixture, and will at last be distributed equally through both vessels. Now, this result cannot, with any shadow of reason, be ascribed to the action of affinity. It is well known that carbonic acid cannot be made to unite either with hydrogen, oxygen, or nitrogen; and, therefore, it is quite gratuitous to assert that it has an affinity for them. Some other power must be in operation, capable of producing the mixture of gases with one another, independently of chemical attraction; and if this power can cause carbonic acid to ascend through a gas which is 22 times lighter than itself, it will surely explain why oxygen and nitrogen, the densities of which differ so little, should mix together in the atmosphere.

The explanation which Mr Dalton has given\* of these phenomena, is founded on the assumption that the particles of one gas, though highly repulsive to each other, do not repel those of a different kind. It follows, from this supposition, that one gas is a vacuum with respect to another; and, therefore, if a vessel full of carbonic acid be made to communicate with another of hydrogen, the particles of each gas insinuate themselves between the particles of the other, till they are equally diffused through both vessels. The particles of the carbonic acid do not indeed fill the space occupied by the hydrogen with the same velocity as if it were a real vacuum, because the particles of the hydrogen afford a mechanical impediment to their progress. The ultimate effect, however, is the same as if the vessel of hydrogen had been a vacuum.

Though it would not be difficult to find objections to this hypothesis, it has the merit of being applicable to every possible case; which cannot, I conceive, be admitted of the other. It accounts, not only for the mixture of gases, but for the equable diffusion of vapours through gases, and through each other.

There is still one circumstance for consideration respecting the atmosphere. Since oxygen is necessary to combustion, to the respiration of animals, and to various other natural operations, by all of which that gas is withdrawn from the air, it is obvious that its quantity would gradually diminish, unless the tendency of those causes was counteracted by some compensating process. To all appearance there does exist some source of compensation; for chemists have not hitherto noticed any change in the constitution of the atmosphere. The only source by which oxygen is known to be supplied, is by the action of growing vegetables. A healthy plant absorbs carbonic acid during the day, appropriates the carbonaceous part of that gas to its own wants, and evolves the oxygen with which it was combined. During the night, indeed, an opposite effect is produced. Oxygen gas then disappears, and carbonic acid is eliminated; but it follows from the ex-

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\* Manchester Memoirs, vol. v.

periments of Priestley and Davy, that plants during 24 hours yield more oxygen than they consume. Whether living vegetables make a full compensation for the oxygen removed from the air by the processes above mentioned, is uncertain. From the great extent of the atmosphere, and the continual agitation to which the different parts of it are subject by the action of winds, the effects of any deteriorating process would be very gradual, and a change in the proportion of its elements could be perceived only by observations made at very distant intervals.

### Compounds of Oxygen and Nitrogen.

Chemists are acquainted with five compounds of nitrogen and oxygen, the composition of which, as deduced from the researches of Gay-Lussac, Dr Henry, and Sir H. Davy, is as follows:

	By Volume.		By Weight.	
	Nitrogen.	Oxygen.	Nitrogen.	Oxygen.
Nitrous oxide	100	50	14	8
Nitric oxide	100	100	14	16
Hyponitrous acid	100	150	14	24
Nitrous acid	100	200	14	32
Nitric acid	100	250	14	40

The first of these compounds, as containing the smallest quantity of oxygen, is presumed to consist of one atom of each element. The atomic weight of nitrogen, that of oxygen being 8, will therefore be 14. The other four compounds must consequently be composed of one atom of nitrogen, united in the second with two, in the third with three, in the fourth with four, and in the fifth with five, atoms of oxygen.

### The Protoxide of Nitrogen.

This gas was discovered by Priestley, who gave it the name of *dephlogisticated nitrous air*. Sir H. Davy called it *nitrous oxide*. According to the principles of chemical nomenclature its proper appellation is *protoxide of nitrogen*. It may be formed by exposing the nitric oxide for some days to the action of iron filings, or other substances which have a strong affinity for oxygen. The nitric oxide loses one half of its oxygen, and is converted into the protoxide. But the most convenient method of procuring it is by means of the nitrate of ammonia. When this salt is exposed to a temperature of 400° or 500° F. it liquefies, bubbles of gas begin to rise from it, and in a short time a brisk effervescence ensues, which continues till the whole of the salt disappears. The nitrate of ammonia should be contained in a glass retort, and the heat applied by means of a lamp placed at such a distance below it as to maintain a moderately rapid evolution of gas.

The sole products of this operation, when carefully conducted, are water and the protoxide of nitrogen. The theory of the process is as follows:—

Nitrate of ammonia is composed of

Nitric acid	54	one proportion.
Ammonia	17	one proportion.

The nitric acid consists of

Nitrogen	14	one proportion.
Oxygen	40	five proportions.
	—	
	54	

And the ammonia of

Nitrogen	14	one proportion.
Hydrogen	3	three proportions.
	—	
	17	

By the action of heat these elements arrange themselves in a new order. The hydrogen takes so much oxygen as is sufficient for forming water, and the residual oxygen converts the nitrogen both of the nitric acid and of the ammonia into the protoxide of nitrogen. The decomposition of 71 grains of the salt will therefore yield

Water	27 or 3 pr.	{ Oxygen	24 or 3 pr.
		{ Hydrogen	3 or 3 pr.
Protoxide of Nitrogen	44 or 2 pr.	{ Oxygen	16 or 2 pr.
	—	{ Nitrogen	28 or 2 pr.
	71		

The protoxide of nitrogen is a colourless gas, which does not affect the blue vegetable colours, even when mixed with atmospheric air. Recently boiled water, which has cooled without exposure to the air, absorbs nearly its own bulk of it at 60° F., and gives it out again unchanged by boiling. The solution, like the gas itself, has a faint agreeable odour and sweet taste. The action of water upon it affords a ready means of testing its purity, removing it readily from all other gases, such as oxygen and nitrogen, which are sparingly absorbed by that liquid. For the same reason it cannot be preserved over cold water; it should be collected either over hot water or mercury.

The protoxide of nitrogen is a supporter of combustion. Most substances burn in it with far greater energy than in the atmosphere. When a recently extinguished candle with a very red wick is introduced into it, the flame is instantly restored. Phosphorus, if previously kindled, burns in it with great brilliancy. Sulphur, when burning feebly, is extinguished by it; but if it is immersed while the combustion is lively, the size of the flame is increased considerably. With an equal bulk of hydrogen it forms a mixture which explodes violently by the electric spark or by flame. In all these cases the product of combustion is the same as when oxygen gas or atmospheric air is used. The protoxide is decomposed; the combustible matter unites with its oxygen, and the nitrogen is set free. The protoxide of nitrogen suffers decomposition when a succession of electric sparks are passed through it. A similar effect is caused by conducting it through a porcelain tube heated to incandescence. It is resolved in both instances, into nitrogen, oxygen, and nitrous acid.

Sir H. Davy discovered\* that the protoxide of nitrogen may be taken into the lungs with safety, and that it supports respiration for a few minutes. He breathed nine quarts of it, contained in a silk bag, for three

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\* Researches on the Nitrous Oxide.

minutes, and 12 quarts for rather more than four; but no quantity could enable him to bear the privation of atmospheric air for a longer period. Its action on the system, when inspired, is very remarkable. A few deep inspirations of it are followed by most agreeable feelings of excitement, similar to the early stages of intoxication. This is shown by a strong propensity to laughter, by a rapid flow of vivid ideas, and an unusual disposition to muscular exertion. These feelings however soon subside, and the person returns to his usual state without experiencing the languor or depression which so universally follows intoxication from spirituous liquors.

The protoxide of nitrogen was analyzed by Sir H. Davy by means of hydrogen gas. He mixed 39 measures of the former with 40 measures of hydrogen, and fired the mixture by the electric spark. Water was formed, and the residual gas, which amounted to 41 measures, had the properties of pure nitrogen. As 40 measures of hydrogen require 20 of oxygen for combustion, it follows that 39 volumes of the protoxide of nitrogen contain 41 of nitrogen and 20 of oxygen. But since no exception has hitherto been found to Gay-Lussac's law of gaseous combination, it may be inferred that the protoxide of nitrogen contains its own bulk of nitrogen and half its volume of oxygen. The recent analysis by Dr Henry, (*Annals of Phil.* vol. viii. N. S.) performed by means of the carbonic oxide gas, has proved beyond doubt that this is the exact proportion. Now,

100 cubic inches of nitrogen weigh	29.652 grains.
50                    do.                    oxygen	16.944

These numbers, added together, amount to 46.596,

which must be the weight of 100 cubic inches of the protoxide; and its specific gravity is therefore 1.5277. Its composition by weight is determined by the same data, being 16.944 of oxygen to 29.652 of nitrogen, or as 8 to 14. Its atomic weight is, of course,  $8 + 14$  or 22.

### *Deutoxide of Nitrogen.*

The deutoxide of nitrogen is best obtained by the action of nitric acid, of specific gravity 1.2, on metallic copper. A brisk effervescence takes place, without the aid of heat, and the gas may be collected over water or mercury. The copper gradually disappears during the process; the liquid acquires a beautiful blue colour, and yields a salt on evaporation, which is composed of nitric acid, and the peroxide of copper. The chemical changes that occur are the following.—One portion of nitric acid suffers decomposition. A part of its oxygen unites with the copper, and converts it into the peroxide of copper; while another part is retained by the nitrogen of the nitric acid, forming the deutoxide of nitrogen. The peroxide of copper attaches itself to some undecomposed nitric acid, and forms the blue nitrate of copper. Many other metals are oxidized by nitric acid, with the disengagement of a similar compound; but none, mercury excepted, yields so pure a gas as copper.

The gas derived from this source was discovered by Dr Hales. It was first carefully studied by Priestley, who called it *nitrous air*. The terms *nitrous gas* and *nitric oxide*, are frequently applied to it; but the *deutoxide of nitrogen*, as indicative of its nature, is the most suitable appellation.

The deutoxide of nitrogen is a colourless gas. When mixed with



atmospheric air, or any gaseous mixture that contains oxygen in an uncombined state, dense, suffocating, acid vapours, of a red or orange-red colour are produced, called nitrous acid vapours; which are copiously absorbed by water, and communicate acidity to it. The deutoxide may be distinguished by this character, from every other substance, and for the same reason affords a convenient test of the presence of free oxygen. Though it gives rise to acid by combining with oxygen, the deutoxide of nitrogen itself does not redden the blue colour of vegetables; but for this experiment, the gas must be well washed with water to separate all traces of nitrous acid. Water absorbs the deutoxide sparingly;—100 measures of that liquid, cold, and recently boiled, take up about 11 of the gas.

Very few inflammable substances can burn in the deutoxide of nitrogen. Burning sulphur, and a lighted candle are instantly extinguished by it. Charcoal and phosphorus, however, if in a state of vivid combustion at the moment of being immersed in it, burn with increased brilliancy. The product of the combustion is carbonic acid in the first case, and phosphoric acid in the second, nitrogen being separated in both instances. With an equal bulk of hydrogen, it forms a mixture which cannot be made to explode, but which is kindled by contact with a lighted candle, and burns rapidly with a white flame. Water and pure nitrogen are the products.

The deutoxide of nitrogen is quite irrespirable, exciting a strong spasm of the glottis, as soon as an attempt is made to inhale it. The experiment, however, is a dangerous one; for if the gas did reach the lungs, it would there mix with atmospheric air, and be converted into nitrous acid vapours, which are highly irritating and corrosive.

The deutoxide of nitrogen is resolved into its elements by being passed through red-hot tubes. A succession of electric sparks have a similar effect. It is converted into the protoxide of nitrogen by substances which have a strong affinity for oxygen, such as iron filings, and the alkaline sulphurets. Its composition was ascertained by Sir H. Davy by the combustion of charcoal. Two volumes of the deutoxide yielded one volume of nitrogen, and about one of carbonic acid\*; whence it was inferred to consist of equal measures of oxygen and nitrogen united without any condensation. Gay-Lussac proved in his paper in the *Memoires d'Arcueil*, that this proportion is rigidly exact. He decomposed 100 measures of the gas, by heating potassium in it; 50 measures of pure nitrogen were left, and the loss of weight corresponded to 50 measures of oxygen. The same fact has been lately proved by Dr Henry in the paper already referred to. From these data, its composition by weight, and its specific gravity may be determined by a simple calculation:—

50 cubic inches of oxygen weigh	16.944 grains.
50 . . . nitrogen	14.826
	<hr/> 31.770

Hence 100 cubic inches of the deutoxide of nitrogen, at the mean temperature and pressure, weigh 31.77 grains; and its specific gravity is therefore 1.0416. This is nearly the mean density of the deutoxide, as determined directly by Davy, Thomson and Bérard, which confirms

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\* Elements of Chemical Philosophy, p. 200.

the accuracy of the data on which the calculation is founded. The elements of the deutoxide are obviously in the ratio, by weight, of 14 nitrogen to 16 oxygen; that is, one atom of the first to two atoms of the second. An atom of the compound is therefore  $14 + 16 = 30$ .

From the invariable formation of the red coloured acid vapours, whenever the deutoxide of nitrogen and oxygen are mixed together, these gases detect the presence of each other with great certainty; and since the product is wholly absorbed by water, one may be entirely removed from any gaseous mixture, by adding a sufficient quantity of the other. Priestley, who first observed this fact, supposed that combination takes place between them only in one proportion; and inferring on this supposition, that a given absorption would always indicate the same quantity of oxygen, he was led to employ the deutoxide of nitrogen in Eudiometry. But in this opinion he was mistaken. The discordant results that were obtained by his method, soon excited suspicion of its fallacy; and the source of it has since been discovered by the researches of Dalton and Gay-Lussac. It appears from the experiments of Gay-Lussac, and his results do not differ materially from those of Mr Dalton, that for 100 measures of oxygen, 400 of the deutoxide may be absorbed as a maximum, and 133 as a minimum; and that between these extremes, the quantity of the deutoxide corresponding to 100 of oxygen, is exceedingly variable. It does not follow from this, that oxygen and the deutoxide of nitrogen can unite in every proportion within these limits. The true explanation is, that the mixture of these gases may give rise to three compounds, the hyponitrous, the nitrous, and the nitric acid; and that either may be formed almost, if not entirely, to the exclusion of the others, if certain precautions are adopted. But in the usual mode of operating, two if not all are generated at the same time, and in a proportion to one another which is by no means uniform. The circumstances that influence the degree of absorption, when a mixture of oxygen and the deutoxide of nitrogen is made over water, are the following:—1, The diameter of the tube; 2, The rapidity with which the mixture is made; 3, The relative proportion of the two gases; 4, The time allowed to elapse after mixing them; 5, Agitation of the tube; and lastly, The opposite conditions of adding the oxygen to the deutoxide, or the deutoxide to the oxygen.

Notwithstanding these many sources of error, Dalton and Gay-Lussac maintain that the deutoxide of nitrogen may nevertheless be employed in eudiometry; and have described the precautions which are required to ensure accuracy. Mr Dalton has given his process in the 10th volume of the *Annals of Philosophy*; and further directions have been published by Dr Henry in his *Elements*. The method of Gay-Lussac, to which my own observation would lead me to give the preference, may be found in the 2d volume, page 247, *Memoires d'Arcueil*. Instead of employing a narrow tube, such as is commonly used for measuring gases, Gay-Lussac advises that 100 measures of air should be introduced into a very wide tube or jar, and that an equal volume of the deutoxide of nitrogen should then be added. The red vapours, which are instantly produced, disappear very quickly, and the absorption, after half a minute, or a minute at the most, may be regarded as complete. The residue is then passed into a graduated tube and measured. The diminution almost always, according to Gay-Lussac, amounts to 84 measures, one-fourth of which is oxygen. Gay-Lussac has applied this process to the analysis of various mixed gases,

in which the oxygen was sometimes in a greater, at others in a less proportion than in the atmosphere, and the indications were always correct. When the proportion of oxygen is great, a proportionably large quantity of the deutoxide must of course be employed, in order that an excess of it might be present.

There is another mode of absorbing oxygen by means of the deutoxide of nitrogen. If a current of the deutoxide be conducted into a solution of the protosulphate of iron, the gas is absorbed in large quantity, and the solution acquires a deep olive-brown colour, which appears almost black when fully saturated. This solution absorbs oxygen with facility. But it cannot be safely employed in eudiometry; because the absorption of oxygen is accompanied, or at least very soon followed, by an evolution of gas from the liquid itself.

Sir H. Davy ascertained that the deutoxide of nitrogen is dissolved directly by the solution of iron, in the cold, without decomposition; and that when the solution is heated, the greater part of the gas is disengaged, and the remainder decomposed. The decomposition is determined chiefly by the affinity of the protoxide of iron for oxygen gas. The protoxide of iron decomposes a portion of water and of the deutoxide of nitrogen at the same time, and unites with the oxygen of both; while the hydrogen of the water, and the nitrogen of the deutoxide combine together, and generate ammonia. Nitric acid is formed when the solution is exposed to the air or oxygen gas, but not otherwise.

### *Hyponitrous Acid.*

On adding an excess of the deutoxide of nitrogen to oxygen gas, confined in a glass tube over mercury, Gay-Lussac observed that the absorption is always uniform, provided a strong solution of pure potash is put into the tube before mixing the two gases. He found that 100 measures of oxygen gas combined under these circumstances with 400 of the deutoxide, forming an acid which unites with the potash. The compound so formed is the hyponitrous acid, the composition of which can be easily inferred from the proportions just mentioned. For as the deutoxide of nitrogen contains half its volume of oxygen gas, the new acid must be composed of 200 measures of nitrogen to 300 of oxygen, or of 100 to 150. It contains, therefore, three times more oxygen than the protoxide of nitrogen; so that, by weight, it is formed of

Nitrogen	14	:	1	atom.
Oxygen	24	:	3	atoms.

and the relative weight of its atom is 38.

Another method of forming the hyponitrous acid is by keeping the deutoxide of nitrogen for three months in a glass tube over mercury, in contact with a concentrated solution of pure potash. The deutoxide is resolved into hyponitrous acid, which unites with the potash, and into the protoxide of nitrogen which remains in the tube.

The hyponitrous acid has not hitherto been obtained in a free state. When an acid is added to the hyponitrite of potash, the hyponitrous acid, instead of being dissolved by the water of the solution, suffers decomposition, and is converted, according to Gay-Lussac, into nitrous acid, and the deutoxide of nitrogen.

*Nitrous Acid.*

To form pure nitrous acid by the mixture of oxygen gas with the deutoxide of nitrogen, the operation must not be conducted over water or mercury. The presence of the former determines the production of nitric acid; the latter is oxidized by the nitrous acid, and therefore decomposes it. Sir H. Davy made this compound by mixing two measures of the deutoxide of nitrogen and one of oxygen, free from moisture, in a dry glass vessel, previously exhausted by the air-pump. (*Elements*, p. 261.) Nitrous acid vapours were produced, and a contraction ensued, amounting to about one-half the volume of the mixed gases. The experiments of Gay-Lussac (*An. de Ch. et de Ph.* vol. i.) were similar in principle. He agrees with Sir H. Davy as to the proportion of the two gases, but is of opinion that they condense, in uniting, to 1-3d of their original volume. The conclusions of those chemists respecting the composition of nitrous acid have been confirmed by the researches of Dulong. (*An. de Ch. et de Ph.* vol. ii.) It is composed therefore of

	<i>By Volume.</i>		<i>By Weight.</i>
Nitrogen	100	:	14 : 1 atom.
Oxygen	200	:	32 : 4 atoms.

and its combining proportion is  $32 + 14 = 46$ .

The nitrous acid vapour is characterized by its orange red colour. It is quite irrespirable, exciting great irritation and spasm of the glottis, even when moderately diluted with air. A taper burns in it with considerable brilliancy. It extinguishes burning sulphur; but the combustion of phosphorus continues in it with great vividness.

Nitrous acid may exist in the liquid as well as in the gaseous form. The liquid acid is most conveniently prepared by exposing the crystallized nitrate of lead, carefully dried, to a heat sufficient to decompose it. The nitric acid of the salt is by this means resolved into nitrous acid and oxygen; and if the products are received in vessels kept moderately cool, the greater part of the former condenses into a liquid. This substance was first obtained by Gay-Lussac, who regarded it as hyponitrous acid, and described it as such in the paper above referred to; but M. Dulong has proved, by a careful analysis, that it is in reality anhydrous nitrous acid. Dulong procured it by mixing the deutoxide of nitrogen and oxygen gases in the ratio of 2 to 1, and exposing the nitrous acid vapours to a low temperature.

The liquid anhydrous acid has the following properties: It is powerfully corrosive, has a strong acid taste and pungent odour, and is of a yellowish orange colour. Its density is 1.451. It preserves the liquid form at the ordinary temperature and pressure, and boils at  $82^{\circ}$  F. Exposed to the atmosphere, it evaporates with great rapidity, forming the common nitrous acid vapours, which, when once mixed with air or other gases, require an intense cold to condense them.

The action of water on the anhydrous nitrous acid is very remarkable. On mixing it with a large quantity of water, it is instantly resolved into nitric acid and the deutoxide of nitrogen; the former unites with the water, making a colourless solution, while the greater part of the latter escapes in the form of gas. When nitrous acid is added to a very small quantity of water, none of the deutoxide is disengaged; and a green-coloured liquid is produced. If, instead of employing a very large or a very small proportion of water, the anhydrous acid be

dropped into a moderate quantity of that fluid, the disengagement of the deutoxide of nitrogen, at first considerable, becomes less and less at each addition of the acid, till at last the evolution of gas ceases altogether. The colour of the solution varies considerably during the experiment. From being quite colourless, the liquid acquires a greenish blue tinge, thence passes into green of various depths of shade, and at length becomes of a yellowish orange,—the colour of the nitrous acid itself.

These changes are of a complicated nature, and may be accounted for in different ways. The following explanation appears to me most consistent with the phenomena. It is founded on the supposition, or rather, as I conceive, upon the fact, that the nitrous and hyponitrous acids cannot exist alone in water, but are always decomposed by that fluid in consequence of its affinity for nitric acid. When a drop of nitrous acid is added to a very small quantity of water, it is resolved into nitric and hyponitrous acids, the latter being protected from decomposition by the former having combined with the water. The hyponitrous acid is therefore mixed with the solution of nitric acid, or is perhaps chemically united with it. On adding a second portion of nitrous acid, that acid is protected from decomposition by the same circumstance which preserves the hyponitrous; and, consequently, it remains in a state of mixture or combination with the two other acids. If the anhydrous nitrous acid be mixed with a large quantity of water, it is converted into nitric acid and the deutoxide of nitrogen; and every successive addition experiences a similar change, till the water has become sufficiently charged with nitric acid to enable the hyponitrous to exist in it. The subsequent additions of nitrous acid will then be converted into nitric and hyponitrous acids, till the affinity of the water for nitric acid is so far satisfied that it can no longer decompose the nitrous acid.

The changes which are produced in the anhydrous nitrous acid by adding successive portions of water, may be anticipated from what precedes. It is resolved into nitric and hyponitrous acids, and into nitric acid and the deutoxide of nitrogen; and when the dilution is considerable, the greater part, if not the whole, of the hyponitrous acid will likewise be decomposed. The colour of the fluid at different periods of the process is attributed to the quantity of the nitrous acid which is dissolved, and the degree of its dilution. It is difficult however to perceive how an orange-coloured liquid should give different shades of green and blue merely by being diluted. May not the blue be caused by the hyponitrous acid, the different shades of green by mixtures of the hyponitrous and nitrous acids, and the yellow and orange by the preponderance of the latter? Some observations of M. Dulong seem to justify this idea, and it is supported by the action of the deutoxide of nitrogen on nitric acid.

Nitrous acid is a powerful oxidizing agent, readily giving oxygen to the more oxidable metals, and to most substances which have a strong affinity for it. The nitrous acid is of course decomposed at the same time; pure nitrogen, and the protoxide of nitrogen, are sometimes evolved, but most commonly it is converted into the deutoxide. When passed through red-hot porcelain tubes, its decomposition is always complete, and a mixture of oxygen and nitrogen gases is obtained.



*Nitric Acid.*

If a succession of electric sparks be passed through a mixture of oxygen and nitrogen gases confined in a glass tube over mercury, a little water being present, the volume of the gases will gradually diminish, and the water after a time will be found to have acquired acid properties. On neutralizing the solution with potash, or what is better, by putting a solution of pure potash instead of water into the tube at the beginning of the experiment, a salt is obtained which possesses all the properties of the nitrate of potash. This experiment was performed by Mr Cavendish in 1785, who inferred from it that nitric acid is composed of oxygen and nitrogen. The best proportion of the gases was found to be seven of oxygen to three of nitrogen; but as some nitrous acid is always formed during the process, the exact composition of nitric acid cannot be determined in this way.

The nitric acid may be formed much more conveniently by adding the deutoxide of nitrogen slowly over water to an excess of oxygen gas. Gay-Lussac proved that the nitric acid might in this manner be obtained quite free from the nitrous or hyponitrous acids; and that it is composed of 100 measures of nitrogen, and 250 of oxygen. This result agrees with the proportion which Sir H. Davy has deduced from his observations; and it is confirmed by an analysis of the nitrate of baryta recently made by Dr Henry. The nitric acid is therefore composed of

	<i>By Volume.</i>		<i>By Weight.</i>			
Nitrogen	.	100	:	14	:	1 atom.
Oxygen	.	250	:	40	:	5 atoms.

and its combining proportion is 54.

Nitric acid cannot exist in an insulated state. The deutoxide of nitrogen and oxygen gases never form nitric acid if mixed together when quite dry; and nitrous acid vapour may be kept in contact with oxygen without change, provided no water is present. The most simple form under which chemists have hitherto procured nitric acid is in solution with water; this, in its concentrated state, is the nitric acid of the pharmacopœia.

The nitric acid of commerce is procured by decomposing some salt of nitric acid by means of concentrated sulphuric acid; and common nitre, as the cheapest of the nitrates, is always employed for the purpose. This salt, previously well dried, is put into a glass retort, and a quantity of the strongest sulphuric acid is poured upon it. On applying heat, ebullition ensues, owing to the escape of nitrous acid vapours, which must be collected in a receiver kept cold by moist cloths. The heat should be steadily increased during the operation, and continued as long as any acid vapours come over.

Chemists differ as to the best proportions for forming nitric acid. The London College recommends equal weights of nitre and sulphuric acid; the Edinburgh and Dublin colleges employ three parts of nitre to two of the acid. The proportion of the London College is so calculated that the potassa of the nitre shall be entirely converted into a bisulphate; for one proportion of nitre (54 nitric acid + 48 potassa) is 102, and 98 corresponds to two atoms of concentrated sulphuric acid. The residue of the Edinburgh process is a mixture of the sulphate and bisulphate of potassa.

There are two substantial reasons for using more than one proportion of sulphuric acid to one of nitre. The first is, that nitre cannot be wholly decomposed by a quantity of sulphuric acid, which is merely sufficient for forming a neutral sulphate. Owing to the tendency of potassa to unite with two proportions of that acid, the product would contain a portion of bisulphate and of undecomposed nitre. The second reason is, that when the neutral sulphate constitutes the greater part of the residue, it forms such a compact and sparingly soluble mass, that it can scarcely ever be removed from the retort without breaking it. But though it is advisable to use more than one atom of sulphuric acid, it is important to employ no more than is really required for decomposing the nitre with advantage. An unnecessary excess is not only uneconomical, but positively hurtful; for some of it is then apt to pass off in vapour during the distillation, and thus render the nitric acid impure. The proportions of the Edinburgh College are calculated to fulfil all these conditions; the excess of sulphuric acid is sufficient to decompose almost all, if not the whole of the nitre, and a pure nitric acid is obtained.

The decomposition of nitre by sulphuric acid does not yield the same product in all its stages. Red fumes appear both at the commencement and towards the close of the process, especially at the latter, owing to the decomposition of a part of the nitric acid, which is converted into oxygen and nitrous acid. For this reason the nitric acid always contains more or less nitrous acid, and therefore its colour varies from a pale straw yellow to a deep orange. If a very pale acid is required, two receivers should be used; one for condensing the colourless vapours of nitric acid, and another for the coloured products. The coloured acid is called nitrous acid by the college; but it is in reality a mixture or compound of nitric and nitrous acids, similar to what may be obtained by mixing the anhydrous nitrous with the colourless nitric acid. It is easy to convert the common mixed acid of the college into the colourless nitric acid, by exposing the former to a gentle heat for some time, when all the nitrous acid will be expelled. But this process is rarely necessary, as the coloured acid may be substituted in almost every case for that which is colourless. Where an acid of great strength is required, the former is even preferable.

Nitric acid frequently contains the sulphuric and muriatic acids. The former is derived from the acid which is used in the process; the latter from the muriate of soda, which is sometimes mixed with nitre. These impurities may be detected by adding a few drops of a solution of muriate of baryta and nitrate of silver to separate portions of nitric acid diluted with three or four parts of distilled water. If the muriate of baryta cause a cloudiness or precipitate, sulphuric acid must be present: if a similar effect be produced by nitrate of silver, the presence of muriatic acid may be inferred. Nitric acid is purified from sulphuric acid by redistilling it from a small quantity of the nitrate of potassa, with the alkali of which the sulphuric acid unites, and remains in the retort. To separate the muriatic acid, it is necessary to drop a solution of nitrate of silver into the nitric acid as long as a precipitate forms, and draw off the pure acid by distillation.

Nitric acid possesses acid properties in an eminent degree. A few drops of it diluted with a considerable quantity of water form an acid solution, which reddens litmus paper permanently. It unites with and neutralizes alkaline substances, forming salts with them which are called nitrates. In its purest and most concentrated state it is colour-

less, and has a specific gravity of 1.50 or 1.510. It still contains a considerable quantity of water, from which it cannot be separated without decomposition, or by uniting with some other body. An acid of density 1.50 contains 25 per cent. of water, according to the experiments of Mr Philips; and 20.3 per cent. according to those of Dr Ure\*. Nitric acid of this strength emits dense, white, suffocating vapours when exposed to the atmosphere. It attracts watery vapour from the air, whereby its specific gravity is diminished. A rise of temperature is occasioned by mixing it with a certain quantity of water. Dr Ure found that when 58 measures of nitric acid, of specific gravity 1.5, are suddenly mixed with 42 of water, the temperature rises from 60 to 140° F.; and the mixture, on cooling to 60°, occupies the space of 92.65 measures instead of 100. From its strong affinity for water, it occasions snow to liquefy with great rapidity; and an intense degree of cold is generated if the mixture be made in due proportion†.

Nitric acid boils at 248° F., and may be distilled without suffering material change. An acid of less specific gravity than 1.42 becomes stronger by being heated, because the water evaporates more rapidly than the acid. An acid, on the contrary, which is stronger than 1.42 is weakened by the application of heat.

Nitric acid may be frozen by cold. The temperature at which congelation takes place varies with the strength of the acid. The strongest acid freezes at about 50 degrees below zero. When diluted with half its weight of water, it becomes solid at  $-1\frac{1}{2}^{\circ}$  F. By the addition of a little more water its freezing point is lowered to  $-45^{\circ}$  F.

Nitric acid acts powerfully on substances which are disposed to unite with oxygen; and hence it is much employed by chemists for bringing bodies to their maximum of oxidation. Nearly all the metals are oxidized by it; and some of them, such as tin, copper, and mercury, are attacked with great violence. If flung on burning charcoal, it increases the brilliancy of its combustion in a high degree. Sulphur and phosphorus are converted into acids by its action. All vegetable substances are decomposed by it. In general the oxygen of the nitric acid enters into direct combination with the hydrogen and carbon of those compounds, forming water with the first, and carbonic acid with the second. This happens remarkably in those compounds in which hydrogen and carbon are predominant, as in alcohol and the oils. It effects the decomposition of animal matters also. The cuticle and nails receive a permanent yellow stain when touched with it; and if applied to the skin in sufficient quantity it acts as a powerful caustic, destroying the organization of the part entirely.

When oxidation is effected through the medium of nitric acid, the acid itself is commonly converted into the deutoxide of nitrogen. This gas is sometimes given off nearly quite pure; but in general some nitrous acid, protoxide of nitrogen, or pure nitrogen is disengaged at the same time. The direct solar light deoxidizes nitric acid, resolving a portion of it into oxygen and nitrous acid. The former separates; the latter is absorbed by the nitric acid, and converts it into the mixed nitrous acid of the shops. When the vapour of nitric acid is passed

\* See his Table in the Appendix, showing the strength of diluted acid of different densities.

† See Table of frigorific mixtures, p. 42.

through red-hot porcelain tubes, it suffers complete decomposition, and a mixture of oxygen and nitrogen gases is the product.

Nitric acid may also be deoxidized by passing a current of the deutoxide of nitrogen through it. That gas, by taking oxygen from the nitric acid, is converted into nitrous acid; and a portion of nitric acid, by losing oxygen, passes into the same compound. The nitrous acid, thus derived from two sources, gives a colour to the nitric acid, the depth and kind of which depend upon the quantity of the deutoxide of nitrogen which has been employed. The first portion communicates a pale straw colour, which gradually deepens as the absorption of the deutoxide continues, till the nitric acid has acquired a deep orange hue, together with all characters of the strong fuming nitrous acid. But the solution still continues to absorb the deutoxide; and in doing so, its colour passes through different shades of olive and green, till it becomes greenish blue. By applying heat to the blue liquid, the deutoxide of nitrogen is evolved; and in proportion as it escapes, the colour of the solution changes to green, olive, orange, and yellow, at length becoming pale as at first. Nitrous acid vapours are likewise disengaged as well as the deutoxide. These phenomena are very favourable to the view that the conversion of the orange colour into olive, green, and blue, is owing to the formation of hyponitrous acid.

All the salts of nitric acid are soluble in water, and therefore it is impossible to precipitate that acid by any reagent. The presence of nitric acid, when uncombined, is readily detected by its strong action on copper and mercury, and by its forming with potassa a neutral salt, which crystallizes in prisms, and which has all the properties of nitre. Gold leaf is a still more delicate test of it. A liquid which contains no chloric acid, and which is unable to dissolve gold leaf, but acquires the property of doing so when pure muriatic acid is added to it, must contain nitric acid. This test is applicable, whether the nitric acid is free, or in combination with alkaline substances.

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## SECTION VI.

### CARBON.

When wood is heated to a certain degree in the open air, it takes fire, and burns with the formation of water and carbonic acid gas till the whole of it is consumed. A small portion of ashes, consisting of the alkaline and earthy matters which had formed a part of the wood, is the sole residue. But if the wood be heated to redness in close vessels, so that the atmospheric air cannot have free access to it, a large quantity of gaseous and other volatile matters is expelled, and a black, hard, porous substance is left, called *charcoal*.

Charcoal may be procured from other sources. When the volatile matters are driven off from coal, as in the process for making coal gas, a peculiar kind of charcoal, called *coke*, remains in the retort. Most animal and vegetable substances yield it when ignited in close vessels. Thus, a very pure charcoal may be procured from starch or sugar; and from the oil of turpentine or spirit of wine, by passing their vapour through tubes heated to redness. When bones are made red-hot in a

covered crucible, a black mass remains, which consists of charcoal mixed with the earthy matters of the bone. It is called *ivory black* or *animal charcoal*.

Charcoal is hard and brittle, conducts heat very slowly, but is a good conductor of electricity. Its density is stated much too low in chemical works:—according to Mr Leslie, its specific gravity is rather greater than that of the diamond. It is quite insoluble in water, is attacked with difficulty by nitric acid, and is little affected by any of the other acids, or by the alkalies. It undergoes little change from exposure to air and moisture, being less injured under these circumstances than wood. It is exceedingly refractory in the fire, if excluded from the air, supporting the most intense heat which chemists are able to produce without change.

Charcoal possesses the property of absorbing a large quantity of air or other gases at common temperatures, and of yielding the greater part of them again when it is heated. It appears from the researches of Saussure, that different gases are absorbed by it in different proportions. His experiments were performed by plunging a piece of red-hot charcoal under mercury, and introducing it when cool into the gas to be absorbed. He found that charcoal prepared from box-wood, absorbs, during the space of 24 or 36 hours, of

Ammoniacal gas	.	.	90 times its volume.
Muriatic acid	.	.	85
Sulphurous acid	.	.	65
Sulphuretted hydrogen	.	.	55
Nitrous oxide	.	.	40
Carbonic acid	.	.	35
Olefiant gas	.	.	35
Carbonic oxide	.	.	9.42
Oxygen	.	.	9.25
Nitrogen	.	.	7.5
Hydrogen	.	.	1.75

The absorbing power of charcoal, with respect to gases, cannot be attributed to chemical action; for the quantity of each gas, which is absorbed, bears no relation whatever to its affinity for charcoal. The effect is in reality owing to the peculiar porous texture of that substance, which enables it, in common with most spongy bodies, to absorb more or less of all gases, vapours, and liquids, with which it is in contact. This property is most remarkable in charcoal prepared from wood, especially in the compact varieties of it, the pores of which are numerous and small. It is materially diminished by reducing the charcoal to powder; and in plumbago, which has not the requisite degree of porosity, it is wanting altogether.

The porous texture of charcoal accounts for the general fact of absorption only; its power of absorbing more of one gas than of another, must be explained on a different principle. This effect, though modified to all appearance by the influence of chemical attraction, seems to depend chiefly on the natural elasticity of the gases. Those which possess such a great degree of elasticity as to have hitherto resisted all attempts to condense them into liquids, are absorbed in the smallest proportion; while those that admit of being converted into liquids by compression, are absorbed more freely. For this reason, charcoal absorbs vapours more easily than gases, and liquids than either.

Messrs Allen and Pepys determined experimentally the increase in



weight experienced by different kinds of charcoal, recently ignited, after a week's exposure to the atmosphere. The charcoal from fir gained 13 per cent.; that from *lignum vitae*, 9.6; that from box, 14; from beech, 16.3; from oak, 16.5; and from mahogany, 18. The absorption is most rapid during the first 24 hours. The substance absorbed is both water and atmospheric air, which the charcoal retains with such force, that it cannot be completely separated from them without exposure to a red heat. Vogel\* has observed that charcoal absorbs oxygen in a much greater proportion from the air than nitrogen. Thus, when recently ignited charcoal, cooled under mercury, was put into a jar of atmospheric air, the residue contained only 8 per cent. of oxygen gas; and if red-hot charcoal be plunged into water, and then introduced into a vessel of air, the oxygen disappears almost entirely. It is said that pure nitrogen may be obtained in this way.

Charcoal likewise absorbs the odoriferous and colouring principles of most animal and vegetable substances. When coloured infusions of this kind are digested with a due quantity of charcoal, a solution is obtained, which is nearly, if not quite colourless. Tainted flesh may be rendered sweet and eatable by this means, and foul water may be purified by filtering through charcoal. The substance commonly employed to decolorize fluids is animal charcoal reduced to a fine powder. It loses the property of absorbing colouring matters by use, but recovers it by being heated to redness.

Charcoal is highly combustible. When strongly heated in the open air, it takes fire, and burns slowly. In oxygen gas, its combustion is lively, and accompanied with the emission of sparks. In both cases it is consumed without flame, smoke, or residue, if quite pure; and carbonic acid gas is the product of its combustion.

The pure inflammable principle, which is the characteristic ingredient of all kinds of charcoal, is called *carbon*. In coke it is in a very impure form. Wood-charcoal contains about 1-50th its weight of alkaline and earthy salts, which constitute the ashes when this species of charcoal is burned. In plumbago, the carbon is combined with a small portion of metallic iron. Charcoal derived from spirit of wine is almost quite pure; and the diamond is carbon in a state of absolute purity.

The diamond is the hardest substance in nature. Its texture is crystalline in a high degree, and its cleavage very perfect. Its primary form is the octahedron. It has a specific gravity of 3.520. Acids and alkalis do not act upon it; and it bears the most intense heat in close vessels without fusing or undergoing any perceptible change. Heated to 14° W., in the open air, it is entirely consumed. Newton first suspected it to be combustible from its great refracting power, a conjecture which was rendered probable by the experiments of the Florentine academicians in 1694, and which was subsequently confirmed by several philosophers. Lavoisier first proved it to contain carbon by throwing the sun's rays, concentrated by a powerful lens, upon a diamond contained in a vessel of oxygen gas. The diamond was consumed entirely, oxygen disappeared, and carbonic acid was generated. It has since been demonstrated by the researches of Guyton-Morveau, Smithson Tennant, Allen and Pepys, and Sir H. Davy, that carbonic acid is the product of its combustion. Guyton-Morveau inferred from

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\* Schweigger's Journal, vol. iv.

his experiments that the diamond is pure carbon, and that charcoal is an oxide of carbon. Tennant burned diamonds by heating them with nitre in a gold tube; and, comparing his own results with those of Lavoisier on the combustion of charcoal, he concluded that equal weights of diamond and pure charcoal, in combining with oxygen, yield precisely equal quantities of carbonic acid. He was thus induced to adopt the opinion that charcoal and the diamond are chemically the same substance; and that the difference in their physical characters is solely dependent on a difference of aggregation\*. This conclusion was confirmed by the experiments of Allen and Pepys†, and Sir H. Davy‡, who compared the product of the combustion of the diamond with that derived from different kinds of charcoal. The latter chemist did indeed observe the production of a minute quantity of water during the combustion of the purest charcoal, indicative of a trace of hydrogen; but its quantity is so exceedingly small, that it cannot be regarded as a necessary constituent. It proves only that a trace of hydrogen is retained with such force by charcoal, that it cannot be expelled by the temperature of ignition.

### Carbonic Acid.

Carbonic acid was discovered by Dr Black in 1757, and described by him in his inaugural dissertation *de Magnesia Alba*, under the name of *fixed air*. He observed the existence of this gas in common limestone and magnesia, and found that it might be expelled from these substances by the action of heat or of acids. He also remarked that the same gas was formed during respiration, fermentation, and combustion. Its composition was first demonstrated synthetically by Lavoisier, who burned carbon in oxygen gas, and obtained carbonic acid as the product. The late Mr Smithson Tennant illustrated its nature analytically by passing the vapour of phosphorus over chalk, or the carbonate of lime, heated to redness in a glass tube. The phosphorus took oxygen from the carbonic acid, charcoal in the form of a light black powder was deposited, and the phosphoric acid, which was formed, united with the lime.

Carbonic acid is most conveniently prepared for the purposes of experiment by the action of muriatic acid, diluted with two or three times its weight of water, on fragments of marble. The muriatic acid unites with the lime, forming a muriate of lime, and carbonic acid gas escapes with effervescence.

Carbonic acid, as thus procured, is a colourless, inodorous, elastic fluid, which possesses all the physical characters of the gases in an eminent degree, and requires a pressure of 36 atmospheres to condense it into a liquid. According to the recent experiments of Dr Thomson, (First Principles, vol. i. p. 143,) 100 cubic inches of it, at 60° F. and when the barometer stands at 30 inches, weigh 46.597 grains; and therefore its specific gravity is 1.5277.

Carbonic acid extinguishes burning substances of all kinds. Bodies, when immersed in it, do not cease to burn from a want of oxygen only. It exerts a positive influence in checking combustion, as appears from the fact, that a candle cannot burn in a gaseous mixture composed of four measures of atmospheric air, and one of carbonic acid.

\* Philos. Trans. for 1797.

† Ibid. 1807.

‡ Ibid. 1814.

It is not better qualified to support the respiration of animals, its presence, even in moderate proportion, being soon fatal. An animal cannot live in air which contains sufficient carbonic acid for extinguishing a lighted candle; and hence the practical rule of letting down a burning taper into old wells or pits before any one ventures to descend. When an attempt is made to inspire pure carbonic acid, a violent spasm of the glottis takes place, which prevents the gas from entering the lungs. If it be so much diluted with air as to admit of its passing the glottis, it then acts as a narcotic poison on the system. It is this gas which has often proved destructive to persons sleeping in a confined room with a pan of burning charcoal.

Carbonic acid is quite incombustible, and cannot be made to unite with an additional portion of oxygen. It is a compound, therefore, in which carbon is in its highest degree of oxidation.

Lime water becomes turbid when brought into contact with carbonic acid. The lime unites with the gas, forming carbonate of lime, which, from its insolubility in water, at first renders the solution milky, and afterwards forms a white flaky precipitate. Hence lime water is not only a valuable test of the presence of carbonic acid, but is frequently used to withdraw it altogether from any gaseous mixture that contains it.

Carbonic acid is absorbed by water. This may be easily demonstrated, by agitating the gas with that liquid, or by leaving a jar full of it inverted over water. In the first case the gas disappears in the course of a minute; in the latter it is absorbed gradually. Recently boiled water dissolves its own volume of carbonic acid at the common temperature and pressure; but it will take up much more if the pressure be increased. The quantity of the gas absorbed is in exact ratio with the compressing force; that is, water dissolves twice its volume when the pressure is doubled, and three times its volume, when the pressure is trebled.

A saturated solution of carbonic acid may be made by passing a stream of the gas through a vessel of cold water during the space of half an hour, or still better by the use of a Woulfe's bottle or Nouth's apparatus, so as to aid the absorption by pressure. Water and other liquids which have been charged with carbonic acid under great pressure, lose the greater part of the gas when the pressure is removed. The effervescence which takes place on opening a bottle of ginger beer, cider, or brisk champaign, is owing to the escape of carbonic acid gas. Water, which is fully saturated with carbonic acid gas, sparkles when it is poured from one vessel into another. The solution has an agreeably acidulous taste, and gives to litmus paper a red stain which is lost on exposure to the air. On the addition of lime-water to it, a cloudiness is produced, which at first disappears, because the carbonate of lime is soluble in an excess of carbonic acid; but a permanent precipitate ensues when the free acid is neutralized by an additional quantity of lime water. The water which contains carbonic acid in solution is wholly deprived of the gas by boiling. Removal of pressure from its surface by means of the air-pump has a similar effect.

The agreeable pungency of beer, porter, and ale, is in great measure owing to the presence of carbonic acid, by the loss of which, on exposure to the air, they become stale. All kinds of spring and well water contain carbonic acid, which they absorb from the atmosphere, and to which they partly are indebted for their pleasant flavour. Boiled water has an insipid taste from the absence of carbonic acid.

A knowledge of the exact composition of carbonic acid gas is of very great importance. The researches of Allen and Pepys, and Sir H. Davy, have proved incontestably that oxygen gas, in combining with carbon, so as to form carbonic acid, suffers no change of volume ; or, in other words, that carbonic acid contains its own volume of oxygen. It hence follows that 100 cubic inches, or 46.597 grains of carbonic acid, consist of 100 cubic inches, or 33.888 grains of oxygen, united with 12.709 grains (46.597—33.888) of carbon.

Now, 12.709 : 33.888 :: 6 : 16.

and since, as will soon appear, 6 is the combining proportion of carbon, carbonic acid is composed of

Carbon	.	6	.	1 proportion,
Oxygen	.	16	.	2 proportions.

By a rule which is given at page 104, it may be calculated that carbon, if supposed to exist in the form of vapour, would have a specific gravity of 0.4166 ; from which it follows, that 100 cubic inches of the vapour of carbon, at 60° F., and when the barometer stands at 30 inches, would weigh 12.709 grains. Consequently, 100 cubic inches of carbonic acid gas are composed of

Oxygen gas	.	100 C. J.
Vapour of Carbon	.	100 C. J.

Carbonic acid is always present in the atmosphere, even at the summit of the highest mountains, or at a distance of several thousand feet above the ground. Its presence may be demonstrated by exposing lime water in an open vessel to the air, when its surface will soon be covered with a pellicle, which is carbonate of lime. The origin of the carbonic acid is obvious. Besides being formed abundantly by the combustion of all substances which contain carbon, the respiration of animals is a fruitful source of it, as may be proved by breathing for a few minutes into lime water ; and it is also generated in all the spontaneous changes to which dead animal and vegetable matters are subject. The carbonic acid proceeding from such sources, is commonly diffused equably through the air ; but when any of these processes occur in low confined situations, as at the bottom of old wells, the gas is then apt to accumulate there, and form an atmosphere called *choke damp*, which is fatal to any animals that are placed in it. These accumulations happily never take place, except when there is some local origin for the carbonic acid ; for example, when it is generated by fermentative processes going on at the surface of the ground, or when it issues directly from the earth, as happens at the Grotto del Cane in Italy, and at Pymont in Westphalia. There is no real foundation for the opinion that carbonic acid can separate itself from the great mass of the atmosphere, and accumulate in a low situation merely by the force of gravity. Such a supposition is contrary to the well-known tendency of gases to diffuse themselves equally through one another. It is also contradicted by observation ; for many deep pits, which are free from putrefying organic remains, though otherwise favourably situated for such accumulations, contain good atmospheric air.

Though carbonic acid is the product of many natural operations, chemists have not hitherto noticed any increase in the quantity which is contained in the atmosphere. The only known process which tends to prevent an increase in its proportion, is that of vegetation. Growing plants purify the air by withdrawing carbonic acid

and yielding an equal volume of pure oxygen in return ; but whether a full compensation is produced by this cause, has not yet been satisfactorily demanded.

Carbonic acid is contained in the earth. Many mineral springs, such as that of Tunbridge, Pyrmont, and Carlsbad, are highly charged with it. In combination with lime it forms extensive masses of rock, which geologists have found to occur in all countries, and in every formation.

Carbonic acid unites with alkaline substances, and the salts so constituted are called carbonates. Its acid properties are feeble, so that it is unable to neutralize completely the alkaline properties of potassa, soda and lithia. For the same reason, all the carbonates, without exception, are decomposed by the muriatic and all the stronger acids ; the carbonic acid is displaced, and escapes in the form of gas.

### *Carbonic Oxide Gas.*

When two parts of well-dried chalk and one of pure iron filings are mixed together, and exposed in a gun-barrel to a red heat, a large quantity of aeriform matter is evolved, which may be collected over water. On examination, it is found to contain two compounds of carbon and oxygen, one of which is carbonic acid, and the other *carbonic oxide*. By washing the mixed gases with lime water, the carbonic acid is absorbed, and the carbonic oxide gas is left in a state of purity.

Priestley discovered this gas by igniting chalk in a gun-barrel, and afterwards obtained it in greater quantity from chalk and iron filings. He supposed it to be a mixture of hydrogen and carbonic acid gases. Its real nature was pointed out by Mr Cruickshank\*, and about the same time by Clément and Désormest†.

Carbonic oxide gas is colourless and insipid. It does not affect the blue colour of vegetables in any way ; nor does it combine, like carbonic acid, with lime or any of the pure alkalies. It is very sparingly dissolved by water. Lime-water does not absorb it, nor is its transparency affected by it.

Carbonic oxide is inflammable. When a lighted taper is plunged into a jar full of that gas, the taper is extinguished ; but the gas itself is set on fire, and burns calmly at its surface with a lambent blue flame. The sole product of its combustion, when the gas is quite pure, is carbonic acid, from which it is certain that it contains no hydrogen.

Carbonic oxide gas cannot support respiration. It acts injuriously on the system ; for if diluted with air, and taken into the lungs, it very soon occasions headach and other unpleasant feelings ; and when breathed pure, it almost instantly causes profound coma.

A mixture of carbonic oxide and oxygen gases may be made to explode by flame, by a red-hot solid body, or by the electric spark. If they are mixed together in the proportion of 100 measures of carbonic oxide and rather more than 50 of oxygen, and the mixture is inflamed in Volta's eudiometer by electricity, so as to collect the product of the combustion, the whole of the carbonic oxide, together with 50 measures of oxygen, disappear, and 100 measures of carbonic acid gas occupy their place. From this fact, which was ascertained by Ber-

\* Nicholson's Journal, 4to Ed. vol. v.

† Annales de Chimie, vol. xxxix.



thollet, and has been amply confirmed by subsequent observation, the exact composition of carbonic oxide gas may be easily deduced. For carbonic acid contains its own bulk of oxygen; and since 100 measures of carbonic oxide with 50 of oxygen form 100 measures of carbonic acid, it follows that 100 of carbonic oxide are composed of 50 of oxygen united precisely with the same quantity of carbon as is contained in 100 measures of carbonic acid. Consequently, the composition of carbonic acid being

<i>By Volume.</i>		<i>By Weight.</i>	
Vapour of carbon	100	Carbon	6
	or		
Oxygen gas	50	Oxygen	16
<hr/>		<hr/>	
100 carbonic acid gas.		22 carbonic acid.	

That of carbonic oxide must be

<i>By Volume.</i>		<i>By Weight.</i>	
Vapour of carbon	100	Carbon	6
	or		
Oxygen gas	50	Oxygen	8
<hr/>		<hr/>	
100 carbonic oxide gas.		14 carbonic oxide.	

		<i>Grains.</i>
Also since 50 cubic inches of oxygen gas weigh		16.944
and 100	of the vapour of carbon	12.709

100 cubic inches of carbonic oxide gas must weigh . 29.653

Its specific gravity is therefore 0.9721; and to be satisfied of the accuracy of the data on which these calculations are founded, it is sufficient to state, that its density, as determined experimentally by Dr Thomson, is 0.9700, and is 0.9727 according to the experiments of Berzelius and Dulong.

No compound of carbon and oxygen is known which contains a less quantity of oxygen than carbonic oxide. For this reason it is regarded as a combination of one proportion of carbon=6 and one of oxygen=8, and carbonic acid of one atom of carbon=6 and two of oxygen=16. The combining proportion of carbonic oxide is therefore 14, and that of carbonic acid 22.

The process for generating carbonic oxide will now be intelligible. The principle of the method is to bring carbonic acid at a red heat in contact with some substance which has a strong affinity for oxygen. This condition is fulfilled by igniting chalk, or any carbonate which can bear a red heat without decomposition, such as the carbonates of baryta, strontia, soda, potassa, or lithia, with half its weight of iron filings or of charcoal. The carbonate is reduced to the caustic state, and the carbonic acid is converted into carbonic oxide by yielding oxygen to the iron or the charcoal. When the first is used, an oxide of iron is the product; when charcoal is employed, the charcoal itself is converted into carbonic oxide. This gas may likewise be generated by heating to redness a mixture of almost any metallic oxide with one-sixth of its weight of charcoal powder. The oxides of zinc, iron, or copper, are the cheapest and most convenient. It may also be formed by passing a current of carbonic acid gas over ignited charcoal. In all these processes it is essential that the ingredients be quite free of

moisture and of hydrogen, otherwise some carburetted hydrogen gas would be generated. The product must always be washed with lime-water to separate it from carbonic acid.

Dr Henry has ascertained that when a succession of electric sparks is passed through carbonic acid confined over mercury, a portion of that gas is converted into carbonic oxide and oxygen. When a mixture of hydrogen and carbonic acid gases is electrified, a portion of the latter yields one half of its oxygen to the former, water is generated, and carbonic oxide produced.

## SECTION VII.

### SULPHUR.

Sulphur occurs as a mineral production in some parts of the earth, particularly in the neighbourhood of volcanoes, as in Italy and Sicily. It is commonly found in a massive state; but is sometimes met with crystallized in the form of an oblique rhombic octahedron. It exists much more abundantly in combination with several metals, such as silver, copper, antimony, lead, and iron. It is procured in large quantity by exposing the common iron pyrites to a red heat in close vessels.

Sulphur is a brittle solid, of a greenish yellow colour, emits a peculiar odour when rubbed, and has little taste. It is a non-conductor of electricity, and is excited negatively by friction. Its specific gravity is 1.99. At the temperature of 190° F. it begins to liquefy; it is in a state of perfect fusion at 220° F., and if then cast into cylindrical moulds, forms the common roll sulphur of commerce. It becomes viscid and acquires a reddish-brown colour when the heat is raised to 300° or 350° F.; and if poured at that temperature into water, it becomes a ductile mass, which may be used for taking the impression of seals.

Fused sulphur has a tendency to crystallize in cooling. A crystalline arrangement is perceptible in the centre of the common roll sulphur; and by good management regular crystals may be obtained. For this purpose, several pounds of sulphur should be melted in an earthen crucible; and when partially cooled, the outer solid crust should be pierced, and the crucible quickly inverted, so that the inner and as yet fluid parts may gradually flow out. On breaking the solid mass, when quite cold, crystals of sulphur will be found in its interior.

Sulphur is very volatile. It begins to rise slowly in vapour even before it is completely fused. At 550° or 600° F. it volatilizes rapidly and condenses again unchanged in close vessels. Common sulphur is purified by this process; and if the sublimation be conducted slowly, the sulphur collects in the receiver in the form of detached crystalline grains, called *flowers of sulphur*. In this state, however, it is not quite pure; for the oxygen of the air within the apparatus combines with a portion of sulphur during the process, and forms sulphurous acid. The acid may be removed by washing the flowers repeatedly with water.

Sulphur is insoluble in water, but unites with it under favourable circumstances, forming the white *hydrate of sulphur*, termed *Lac Sul.*

*phuris*. It dissolves readily in boiling oil of turpentine. The solution has a reddish brown colour like melted sulphur, and if fully saturated deposits numerous small crystals in cooling. Sulphur is also soluble in alcohol, if both substances are brought together in the form of vapour. The sulphur is precipitated from the solution by the addition of water.

Sulphur, like charcoal, retains a portion of hydrogen so obstinately that it cannot be wholly freed from it either by fusion or sublimation. Sir H. Davy detected its presence by exposing sulphur to the strong heat of a powerful galvanic battery, when some sulphuretted hydrogen gas was disengaged. The hydrogen from its minute quantity, can only be regarded in the light of an accidental impurity, and as nowise essential to the nature of sulphur.

When sulphur is heated in the open air to 300° F. or a little higher, it kindles spontaneously, and burns with a faint blue light. In oxygen gas its combustion is far more vivid; the flame is much larger and of a bluish-white colour. Sulphurous acid is the product in both instances;—no sulphuric acid is formed even in oxygen gas unless moisture is present.

### *Compounds of Sulphur and Oxygen.*

Chemists are at present acquainted with four compounds of sulphur and oxygen, all of which have acid properties. Their composition is shown by the following table.

	<i>Sulphur.</i>	<i>Oxygen.</i>	<i>S.</i>	<i>Ox.</i>
Hyposulphurous acid	16	8	1	1
Sulphurous acid	16	16	1	2
Sulphuric acid	16	24	1	3
Hyposulphuric acid	32	40	2	5

### *Sulphurous Acid Gas.*

Pure sulphurous acid, at the common temperature and pressure, is a colourless transparent gas, which was first obtained in a separate state by Priestley\*. It is the sole product when sulphur burns in air or in dry oxygen gas, and is the cause of the peculiar odour emitted by that substance during its combustion. It may also be prepared by depriving sulphuric acid of one proportion of its oxygen. This may be done in several ways. If chips of wood, straw, or cork, oil, or other vegetable matters, be heated in strong sulphuric acid, the carbon and hydrogen of those substances deprive the acid of a part of its oxygen, and convert it into sulphurous acid. Nearly all the metals, with the aid of heat, have a similar effect. One portion of sulphuric acid yields oxygen to the metal, and is thereby converted into sulphurous acid; while the metallic oxide, at the moment of its formation, unites with some of the undecomposed sulphuric acid. The best method of obtaining pure sulphurous acid gas is by putting two parts of mercury and three of sulphuric acid into a glass retort, the beak of which is received under mercury, and heating the mixture by an Argand lamp. Effervescence soon takes place, a large quantity of pure sulphurous acid is disengaged, and the sulphate of the oxide of mercury remains in the retort.

Sulphurous acid gas is distinguished from all other gaseous fluids by

\* Priestley on Air, vol. ii. p. 1.

its suffocating pungent odour. All burning bodies, when immersed in it, are extinguished, without setting fire to the gas itself. It is fatal to all animals which are placed in it. A violent spasm of the glottis takes place, by which the entrance of the gas into the lungs is prevented; and even when diluted with air, it excites cough, and causes a peculiar uneasiness about the chest.

Recently boiled water dissolves about 33 times its volume of sulphurous acid, at 60° F. and 30 inches of the barometer, forming a solution which has the peculiar odour of that compound, and from which the gas may be expelled by ebullition, without change.

Sulphurous acid has considerable bleaching properties. It reddens litmus paper, and then slowly bleaches it. Most vegetable colouring matters, such as that of the rose and the violet, are speedily removed, without being first reddened by it. It is remarkable, that the colouring principle is not destroyed by the sulphurous acid; it may be restored either by a stronger acid or by an alkali.

Sir H. Davy inferred from his experiments on the combustion of sulphur in dry oxygen gas, (Elements, p. 273,) that the volume of the oxygen is not altered during the process, a fact which is now admitted by most chemists; so that 100 cubic inches of sulphurous acid contain 100 cubic inches of oxygen. According to Dr Thomson, (Annals of Philosophy, vol. xvi.) sulphurous acid gas is just twice as heavy as oxygen; and the experiments of Davy and of Thénard correspond very closely with his result. It follows, therefore, that sulphurous acid consists of equal weights of sulphur and oxygen; and consequently that 100 cubic inches weigh 67.776 grains, and contain 33.888 grains of sulphur. This proportion is also established by the researches of Berzelius. (An. de Ch. et de Ph. vol. v.)

By the formula, page 104, it may be calculated that the specific gravity of the vapour of sulphur is the same as that of oxygen gas, or 1.1111; and hence 100 cubic inches of that vapour must weigh 33.888 grains. From this it is manifest, that 100 cubic inches of sulphurous acid gas are composed of

Vapour of sulphur	.	.	100 cubic inches.
Oxygen	.	.	100 do.

The specific gravity of sulphurous acid gas is of course double that of oxygen, or 2.2222.

It is inferred from the composition of hyposulphurous acid, sulphuretted hydrogen, and other compounds of sulphur, that 16 is the number which expresses the combining proportion of that substance. Hence sulphurous acid is composed of 16 or 1 proportion of sulphur, and 16 or 2 proportions of oxygen. Its atomic weight is therefore 32.

Though sulphurous acid cannot be made to burn by the approach of flame, it has a very strong attraction for oxygen, uniting with it under favourable circumstances, and forming sulphuric acid. The presence of moisture is essential to this change. A mixture of sulphurous acid and oxygen gases, if quite dry, may be preserved over mercury for any length of time without acting on each other. But if a little water be admitted, the sulphurous acid gradually unites with oxygen, and disappears entirely. For this reason, a solution of sulphurous acid in water cannot be kept unless the atmospheric air is carefully excluded. Many of the chemical properties of sulphurous acid are owing to its affinity for oxygen. On being added to a solution of the peroxide of iron, it takes oxygen, and thus converts the peroxide into the protoxide of that metal. The solutions of metals which have a weak affinity

for oxygen, such as gold, platinum, and mercury, are completely decomposed by it, those substances being precipitated in the metallic form. Nitric acid converts it instantly into sulphuric acid by yielding some of its oxygen. The peroxide of manganese causes a similar change, and is itself converted into the protoxide of manganese which unites with the sulphuric acid.

Sulphurous acid gas may be passed through red-hot tubes without decomposition. Several substances which have a strong affinity for oxygen, such as hydrogen, carbon, and potassium, decompose it at the temperature of ignition.

Of all the gases, sulphurous acid is most readily liquefied by compression. According to Mr Faraday, it is condensed by a force equal to the pressure of two atmospheres. M. Bussy (Annals of Phil. vol. viii. N. S.) has obtained it in a liquid form under the usual atmospheric pressure, by passing it through tubes surrounded by a freezing mixture of snow and salt. The anhydrous liquid acid has a density of 1.45. It boils at 14° F. From the rapidity of its evaporation at common temperatures, it may be used advantageously for producing an intense degree of cold. M. Bussy succeeded in freezing mercury, and liquefying several of the gases, by employing it with this intention.

Sulphurous acid combines with metallic oxides, and forms salts which are called sulphites.

### Sulphuric Acid.

Sulphuric acid was discovered by Basil Valentine towards the close of the 15th century. It is procured for the purposes of commerce by two methods. The first is the process which has been pursued many years in the manufactory at Nordhausen in Germany, and consists in decomposing the sulphate of the protoxide of iron (green vitriol) by heat. The crystallized protosulphate of iron contains seven atoms of water of crystallization; and when strongly dried by the fire, it crumbles down into a white powder, which, according to Dr Thomson, contains one atom of water. On exposing this dried protosulphate of iron to a red heat, the whole of the sulphuric acid is expelled, the greater part of it passing over unchanged into the receiver, in combination with the water of the salt. One portion of the acid is resolved by the strong heat employed in the distillation into sulphurous acid and oxygen. The former escapes as gas throughout the whole process; the latter only in the middle and latter stages, being retained, in the beginning of the distillation, by the protoxide of iron. The peroxide of iron is the sole residue.

The acid, as procured by this process, is a dense, oily, colourless liquid, which emits copious white vapours on exposure to the air, and is hence called *fuming sulphuric acid*. Its specific gravity is stated at 1.896 and 1.90.

From the analysis of Dr Thomson it is composed of

Anhydrous sulphuric acid	.	80	.	2 proportions.
Water	.	9	.	1

On putting this acid into a glass retort, to which a receiver surrounded by snow is securely adapted, and applying a very gentle heat to it, a transparent colourless vapour passes over, which condenses into a white crystalline solid. This substance is shown by the experiments of Thomson, Ure, and Bussy, to be pure anhydrous sulphuric acid. It is tough and elastic; liquefies at 66° F. and boils at a



temperature between  $104^{\circ}$  and  $122^{\circ}$  F., forming, if no moisture is present, a transparent vapour. Exposed to the air, it unites with watery vapour, and flies off in the form of dense white fumes. The residue of the distillation is no longer fuming, and is in every respect similar to the common acid of commerce.

The second process for forming sulphuric acid, which is practised in Britain and in most parts of the Continent, is by burning sulphur previously mixed with one-eighth of its weight of nitrate of potassa. The mixture is burned in a furnace so contrived that the current of air which supports the combustion, conveys the gaseous products into a large leaden chamber, the bottom of which is covered to the depth of several inches with water. The nitric acid yields oxygen to a portion of sulphur, and converts it into sulphuric acid, which combines with the potassa of the nitre; while the greater part of the sulphur forms sulphurous acid by uniting with the oxygen of the air. The nitric acid, in losing oxygen, is converted into the deutoxide of nitrogen, which, by mixing with air at the moment of its separation, gives rise to the red nitrous acid vapours. The gaseous substances present in the leaden chamber, are therefore sulphurous and nitrous acids, atmospheric air and watery vapour. The explanation of the mode in which these substances react on one another so as to form sulphuric acid, was suggested by Clément and Désormes, (*An. de Ch.* vol. lix.) and the subject has been put in a still clearer light by Sir H. Davy, (*Elements*, p. 276.) On mixing together dry sulphurous acid gas and nitrous acid vapour in a glass vessel quite free from moisture, no change ensues; but if a drop of water be added, so as to fill the space with vapour, a white crystalline solid is formed, which is composed of water and the two acids. When these crystals come into contact with water, the sulphurous acid takes oxygen from the nitrous acid, the deutoxide of nitrogen escapes with effervescence, and the sulphuric acid is dissolved by the water.

A similar change takes place within the leaden chamber. The crystalline solid is decomposed by the water at the bottom of the chamber, by which sulphuric acid is generated, and the deutoxide of nitrogen set free. That gas, in mixing with atmospheric air, is again converted into nitrous acid, and thus gives rise to the formation of a second portion of the crystalline solid, which is resolved, like the preceding, into sulphuric acid and the deutoxide of nitrogen. These successive combinations and decompositions continue till the water is sufficiently charged with sulphuric acid, when it is drawn off and concentrated by evaporation.

It hence appears that the oxygen by which the sulphurous is converted into the sulphuric acid, is in reality supplied by the air; and that the combination is effected, not directly, but through the medium of the nitrous acid. The decomposition of the crystalline solid by water seems owing to the affinity of the water for sulphuric acid.

Sulphuric acid, as thus prepared, is never quite pure. It contains some sulphate of potash and of lead, the former derived from the nitre employed in making it, the latter from the leaden chamber. To separate these impurities, the acid should be distilled from a glass or platinum retort. The former may be used with safety by putting some fragments of platinum leaf into it, which causes the acid to boil freely on the application of heat without danger of breaking the vessel.

Pure sulphuric acid, as obtained by the second process, is a dense, colourless, oily fluid, which boils at  $620^{\circ}$  F., and has a specific gravity,

in its most concentrated form, of 1.847 or a little higher, never exceeding 1.850. It is one of the strongest acids with which chemists are acquainted. When undiluted it is powerfully corrosive. It decomposes all animal and vegetable substances by the aid of heat, causing deposition of charcoal and formation of water. It has a strong sour taste, and reddens litmus paper, even though greatly diluted. It unites with alkaline substances, and separates all other acids more or less completely from their combinations with the alkalies.

Sulphuric acid has a very great affinity for water, and unites with it in every proportion. The combination takes place with the production of an intense heat. When four parts by weight of the acid are suddenly mixed with one of water, the temperature of the mixture rises, according to Dr Ure, to 300° F. By its attraction for water it causes the sudden liquefaction of snow; and if mixed with it in due proportion, (p. 42) an intense degree of cold is generated. It absorbs watery vapour with avidity from the air, and on this account is employed in the process for freezing water by its own evaporation. The operation of sulphuric acid in destroying the texture of the skin, in forming ethers, and in decomposing animal and vegetable substances in general, seems dependant on its affinity for water.

The sulphuric acid of commerce freezes at  $-15^{\circ}$  F. Diluted with water so as to have a specific gravity of 1.78 it congeals even above  $32^{\circ}$  F., and remains in the solid state, according to Mr Keir, till the temperature rises to  $45^{\circ}$  F. When mixed with rather more than its weight of water, its freezing point is lowered to  $-36^{\circ}$  F.

When sulphuric acid is passed through a small porcelain tube heated to redness, it is entirely decomposed; and Gay-Lussac found that it is resolved into two measures of sulphurous acid and one of oxygen. Hence it follows that real sulphuric acid is composed of

	<i>By Weight.</i>			<i>By Volume.</i>	
Sulphur	.	16	.	1 p. or vapour of sulphur	100
Oxygen	.	24	.	3 p.	150

and its atomic weight is 40. Berzelius ascertained its composition by converting a known weight of sulphur into sulphuric acid; and his result confirms the conclusion of Gay-Lussac.

Chemists possess an unerring test of the presence of sulphuric acid. If a solution of muriate of baryta is added to a liquid containing sulphuric acid, it causes a white precipitate, the sulphate of baryta, which is characterized by its insolubility in acids and alkalies.

Sulphuric acid does not occur free in nature, except occasionally in the neighbourhood of volcanoes. In combination, particularly with lime and baryta, it is very abundant.

*Hyposulphurous acid.*—This acid may be formed in several ways:—1. By digesting sulphur in a solution of any sulphite; 2. by the digestion of iron filings in a solution of sulphurous acid; 3. by passing a current of sulphurous acid into a solution of the hydrosulphuret of lime or strontia. In the first case, the sulphurous acid takes up an additional quantity of sulphur, and a salt of hyposulphurous acid is obtained; in the second, the sulphurous acid yields one half of its oxygen to the iron, and a hyposulphite of the protoxide of iron is generated; and in the third, the sulphurous acid is deprived of one half of its oxygen by the hydrogen of the sulphuretted hydrogen, pure sulphur is precipitated, and a hyposulphite of lime or of strontia remains in solution.

The salts of hyposulphurous acid were first described by Gay-Lussac in the 85th vol. of the *Annales de Chimie*, under the name of the *Sulphuretted Sulphites*. Its real nature was first explained by Dr Thomson in his *System of Chemistry*, and the researches of Mr Herschel (*Edin. Philos. Journal*, vol. i. pages 8 and 396) leave no doubt of the accuracy of his opinion. On exposing the hyposulphite of lime to a red heat, Mr Herschel found that free sulphur is given off, and that a sulphite of lime remains, the acid of which contains a quantity of sulphur equal to what is expelled during the experiment. It hence follows that the hyposulphurous contains twice as much sulphur as the sulphurous acid, or is composed of

Sulphur	.	16	.	one p.
Oxygen	.	8	.	one p.

and therefore the weight of its atom is 24.

Hyposulphurous acid cannot exist permanently in a free state. On decomposing a hyposulphite by any stronger acid, such as the sulphuric or muriatic, the hyposulphurous acid, at the moment of quitting the base, resolves itself into sulphurous acid and sulphur. All hyposulphites may be known by this character. Mr Herschel succeeded in obtaining free hyposulphurous acid, by adding a slight excess of sulphuric acid to a diluted solution of the hyposulphite of strontia; but its decomposition very soon took place, even at common temperatures, and was instantly effected by heat.

*Hyposulphuric acid.*—The hyposulphuric acid was discovered in 1819, by Welter and Gay-Lussac, who published their description of it in the 10th vol. of the *An. de Ch. et de Physique*. It is formed by passing a current of sulphurous acid gas through water containing peroxide of manganese in fine powder. The manganese yields oxygen to the sulphurous acid, thus converting one part of it into sulphuric, and another part into the hyposulphuric acid, both of which unite with the protoxide of manganese. To the liquid, after filtration, a solution of pure baryta is added in slight excess, which precipitates the protoxide of manganese, and forms an insoluble sulphate of baryta with the sulphuric, and a soluble hyposulphate with the hyposulphuric acid. The hyposulphate of baryta is then decomposed by a quantity of sulphuric acid exactly sufficient for precipitating the baryta, and the hyposulphuric acid is left in solution.

This compound reddens litmus paper, has a sour taste, and forms neutral salts with the alkalis. It has no odour, by which circumstance it is distinguished from sulphurous acid. It cannot be confounded with the sulphuric acid; for it forms soluble salts with baryta, strontia, lime, and the oxide of lead, whereas the compounds which sulphuric acid forms with those bases are all insoluble. The hyposulphuric acid cannot be obtained free from water. Its solution, if confined with a vessel of sulphuric acid under the exhausted receiver of an air-pump, may be concentrated till it has a density of 1.347; but if an attempt is made to condense it still further, the acid is decomposed, sulphurous acid gas escapes, and sulphuric acid remains in solution. A similar change is still more readily produced if the evaporation is conducted by heat.

Welter and Gay-Lussac analyzed the hyposulphuric acid by applying heat to the neutral hyposulphate of baryta. At a temperature a little above 212° F., this salt suffers complete decomposition; sulphurous acid gas is disengaged, and a neutral sulphate of baryta is obtain-

ed. They ascertained in this way, that 72 grains of hyposulphuric acid yield 32 grains of sulphurous, and 40 of sulphuric acid, from which it is probable that the hyposulphuric acid is composed of an atom of each of those acids, combined directly with one another. Regarded as a definite compound of sulphur and oxygen, its composition is,

Sulphur	.	.	32	2 atoms.
Oxygen	.	.	40	5 atoms.

Its combining proportion, whichever opinion is adopted, is 72.

## SECTION VIII.

### *PHOSPHORUS.*

Phosphorus was discovered about the year 1669 by Brandt, an alchemist of Hamburgh. It was originally prepared from urine; but Scheele afterwards described a method of obtaining it from bones. The object of both processes is to bring phosphoric acid in contact with charcoal at a strong red heat. The charcoal takes oxygen from the phosphoric acid; carbonic acid is disengaged, and phosphorus is set free. When urine is employed, the phosphoric acid contained in it should be separated by a solution of the acetate of lead. The phosphate of lead subsides, which, if heated to redness with one-fourth of its weight of powdered charcoal, yields phosphorus readily. If bones are to be used, they should first be ignited in an open fire till they become quite white, so as to destroy all the animal matter they contain, and oxidize the carbon proceeding from its decomposition. The calcined bones, of which the phosphate of lime constitutes nearly four-fifths, should be reduced to a fine powder, and be digested for a day or two with half their weight of concentrated sulphuric acid, so much water being added to the mixture as to give it the consistence of a thin paste. The phosphate of lime is decomposed by the sulphuric acid, and two new salts are generated,—the insoluble neutral sulphate, and the soluble biphosphate of lime. On the addition of boiling water the biphosphate is dissolved, and may be separated by filtration from the sulphate of lime. The solution is then evaporated to the thickness of syrup, mixed with one-fourth of its weight of charcoal in powder, and is heated in an earthen retort well luted with clay. The beak of the retort is put into water, in which the phosphorus, as it passes over in the form of vapour, is collected. When first obtained, it is frequently of a reddish-brown colour, owing to the presence of the phosphuret of carbon, which is generally formed during the process. It may be purified by being put into hot water, and pressed while liquid through chamois leather; or the purification may be rendered still more complete by a second distillation.

Pure phosphorus is transparent and almost colourless. It is so soft that it may be cut with a knife, and the cut surface has a waxy lustre. At the temperature of 108° F. it fuses, and at 550° F. it sublimes.

Phosphorus is exceedingly inflammable. Exposed to the air at common temperatures, it undergoes a slow combustion; it emits a white vapour of a peculiar alliaceous smell, appears distinctly lumi-

nous in the dark and is gradually consumed. On this account phosphorus should always be kept under water. The disappearance of oxygen which accompanies these changes is shown by putting a stick of phosphorus in a jar full of air, inverted over water. The volume of the gas gradually diminishes, and if the temperature of the air is at  $60^{\circ}$  F., the whole of the oxygen will be withdrawn in the course of 12 or 24 hours. The residue is nitrogen, containing about 1-40th of its bulk of the vapour of phosphorus. It is remarkable that the slow combustion of phosphorus does not take place in pure oxygen, unless its temperature be about  $80^{\circ}$  F.; but if the oxygen is rarefied by diminished pressure, or diluted with nitrogen, hydrogen, or carbonic acid, then the oxidation occurs at  $60^{\circ}$  F.

A very slight degree of heat is sufficient to inflame phosphorus. Gentle pressure between the fingers, friction, or a temperature not much above its point of fusion kindles it readily. It burns rapidly even in the air, emitting a splendid white light, and causing an intense heat. Its combustion is far more rapid in oxygen gas, and the light proportionably more vivid.

### *Compounds of Phosphorus and Oxygen.—Phosphoric Acid.*

Of the compounds of phosphorus and oxygen, *phosphoric acid* is by far the most interesting and important. This acid may be obtained in a state of perfect purity by burning phosphorus in air or oxygen gas. Copious white vapours are produced, which fall to the bottom of the vessel like flakes of snow. In this state it is the solid anhydrous phosphoric acid. From its powerful affinity for water, it attracts watery vapour rapidly from the atmosphere, and in the course of two or three minutes appears in the form of minute drops of liquid, which is a solution of phosphoric acid in water.

Phosphoric acid may be conveniently formed by the action of nitric acid on phosphorus. The phosphorus takes oxygen from the nitric acid, and a large quantity of the deutoxide of nitrogen is disengaged; but as the reaction is apt to be very violent, the process ought to be conducted with caution. It is best done by adding fragments of phosphorus to concentrated nitric acid contained in a platinum capsul. A gentle heat is applied so as to commence, and when necessary, to maintain a moderate effervescence; and when one portion of phosphorus disappears, another is added, till the whole of the nitric acid is exhausted. The solution is then evaporated to dryness.

Phosphoric acid may be prepared at a much cheaper rate from bones. For this purpose, the biphosphate of lime, obtained in the way already described, should be boiled for a few minutes with an excess of the carbonate of ammonia. The lime is thus precipitated as a carbonate, and the solution contains phosphate, together with a little sulphate of ammonia. The liquid, after filtration, is evaporated to dryness, and then ignited in a platinum crucible by which the ammonia and sulphuric acid are expelled.

Solid phosphoric acid unites with water in every proportion, and forms, if concentrated, a dense oily liquid. On heating the solution in a platinum vessel, the greater part of the water is driven off; the residue fuses at a low red heat, and concretes on cooling into a brittle glass, called *glacial phosphoric acid*. This substance is a hydrate of phosphoric acid, which cannot be decomposed by the fire; for on



exposing it to a strong red heat, with the view of expelling the water, the compound itself is volatilized. According to Dulong, it is composed of 84 or three atoms of phosphoric acid, and nine or one atom of water.

Phosphoric acid is intensely sour to the taste, reddens litmus paper strongly, and neutralizes the alkalies. It is therefore a powerful acid; but it does not destroy the texture of the skin like the sulphuric and nitric acids. It may be distinguished from all other acids by the following circumstances:—that when carefully neutralized by pure carbonate of soda or potash, it forms a solution in which no precipitate or change of colour is produced when a stream of sulphuretted hydrogen gas is passed through it; but which is precipitated white by a solution of the acetate of lead, and yellow by the nitrate of silver. The first precipitate, the phosphate of lead, dissolves completely on the addition of nitric or phosphoric acid; the second, the phosphate of silver, is dissolved by both those acids, and also by ammonia.

The composition of phosphoric acid has been investigated by Sir H. Davy, Dr Thomson, Berzelius, and M. Dulong. The subject is one of much difficulty, and the results of the two former chemists differ widely from those of the two latter. Dr Thomson infers\* from experiments made by Sir H. Davy and himself, (and his estimate is generally adopted in this country,) that phosphoric acid is composed of

Phosphorus	.	12	.	1 atom.
Oxygen	.	16	.	2 atoms.
<hr/>				
28				

and, consequently, its equivalent is 28.

*Phosphorous acid.*—When phosphorus is heated in highly rarefied air, an imperfect oxidation ensues, and the phosphoric and phosphorous acids are both generated, the latter being obtained in the form of a white volatile powder. In this state it is anhydrous. Heated in the open air, it takes fire, and forms phosphoric acid; but if exposed to heat in close vessels it is resolved into phosphoric acid and phosphorus. It dissolves readily in water, has a sour taste, and smells somewhat like garlic. It unites with alkalies, and forms salts which are termed phosphites. The solution of phosphorous acid absorbs oxygen slowly from the air, and is converted into phosphoric acid. From its tendency to unite with an additional quantity of oxygen, it is a powerful deoxidizing agent; and hence, like sulphurous acid, precipitates mercury, silver, platinum, and gold, from their saline combinations in the metallic form. Nitric acid, of course, converts it into phosphoric acid.

Phosphorous acid may be procured more conveniently by subliming phosphorus through powdered corrosive sublimate, (a compound of chlorine and mercury,) contained in a glass tube†. A limpid liquid comes over which is a compound of chlorine and phosphorus. When this substance is put into water, a peculiar change occurs. A portion of water is decomposed; its hydrogen unites with the chlorine, and forms muriatic acid; while the oxygen attaches itself to the phosphorus, by which phosphorous acid is produced. The solution is

\* First Principles, vol. i. p. 203.

† Davy's Elements, p. 288.

then evaporated to the consistence of syrup to expel the muriatic acid; and the residue, which is the hydrate of phosphorous acid, becomes a crystalline solid on cooling. It inflames when gently heated in the open air, and has all the properties of phosphorous acid.

Phosphorous acid is also generated during the slow oxidation of phosphorus in atmospheric air. The product attracts moisture from the air, and forms an oily-like liquid. M. Dulong thinks that a distinct acid is generated in this case, which he calls *phosphatic acid*; but the opinion of Sir H. Davy, that it is merely a mixture of phosphoric and phosphorous acids, is, I conceive, correct.

With respect to the composition of phosphorous acid, Sir H. Davy ascertained, by careful experiment, that it contains one half less oxygen than phosphoric acid; from which it follows that it is composed of

Phosphorus	.	12	.	one atom.
Oxygen	.	8	.	one atom.

So that its atomic weight is . 20.

*Hypophosphorous acid.*—This acid was discovered in 1816 by M. Dulong\*, and is produced by the action of water on the phosphuret of baryta. The water suffers decomposition; its elements unite with different portions of phosphorus, by which three compounds, phosphuretted hydrogen, phosphoric acid, and hypophosphorous acid, are generated. The first escapes in the form of gas; the two latter combine with the baryta. The hypophosphite of baryta, being soluble, dissolves in the water, and may consequently be separated by filtration from the phosphate of baryta, which is insoluble. On adding a sufficient quantity of sulphuric acid for precipitating the baryta, the hypophosphorous acid is obtained in a free state. On evaporating the solution, a viscid liquid remains, highly acid and uncrystallizable, which is a *hydrate of hypophosphorous acid*. When an attempt is made to expel the water by heat, the acid itself, and some of the water, are decomposed; phosphuretted hydrogen gas is disengaged, a little phosphorus sublimes, and phosphoric acid is left.

The hypophosphorous acid is a powerful deoxidizing agent. It unites with alkaline bases; and it is remarkable that all its salts are soluble in water. The hypophosphites of potash, soda and ammonia, dissolve in every proportion in rectified alcohol; and the hypophosphite of potash is even more deliquescent than the muriate of lime. They are all decomposed by heat, and yield the same products as the acid itself.

M. Dulong determined the proportion of its elements by converting it into phosphoric acid by means of chlorine. He infers from his analysis that it contains 27.25 per cent. of oxygen; but according to Sir H. Davy, it has exactly one half less oxygen than the phosphorous acid, and is therefore composed of

Phosphorus	.	24	.	2 atoms.
Oxygen	.	8	.	1 atom.

*Oxides of phosphorus.*—Chemists have not yet succeeded in proving the existence of any oxide of phosphorus. When phosphorus is kept under water for some time, a white film forms upon its surface, which

\* Mem. d'Arcueil, vol. iii. or An. de Ch. et de Physique, vol. ii.

some have regarded as an oxide of phosphorus. The red-coloured matter, which remains after the combustion of phosphorus, is also supposed to be an oxide. The nature of these substances has not, however, been determined in a satisfactory manner.

## SECTION IX.

### BORON.

Sir H. Davy discovered the existence of *Boron*, in 1808, by exposing boracic acid to the action of a powerful galvanic battery; but he did not obtain a sufficient supply of it for determining its properties. It was procured in greater quantity by Gay-Lussac and Thénard\* in 1808, by heating boracic acid with potassium. The boracic acid is by this means deprived of its oxygen, and boron is set free.

Boron is a dark olive-coloured substance, which has neither taste nor smell, and is a non-conductor of electricity. It is insoluble in water, alcohol, ether, and oils. It does not decompose water whether hot or cold. It bears an intense heat in close vessels, without fusing or undergoing any other change, except a slight increase of density. Its specific gravity is about twice as great as that of water. It may be exposed to the atmosphere at common temperatures without change; but if heated to 600° F., it suddenly takes fire, oxygen gas disappears, and boracic acid is generated. It experiences a similar change when heated in nitric acid, or with any substance that yields oxygen with facility.

*Boracic acid.*—This is the only known compound of boron and oxygen. As a natural product it is found in the hot springs of Lipari, and in those of Sasso in the Florentine territory. It is a constituent of several minerals, among which the datolite and boracite may in particular be mentioned. It occurs much more abundantly under the form of borax, a native compound of boracic acid and soda. It is prepared for chemical purposes by adding sulphuric acid to a concentrated solution of purified borax in boiling water, till the liquid acquires a distinct acid reaction. The sulphuric acid unites with the soda; and the boracic acid is deposited, when the solution cools, in a confused group of crystals, which are sometimes scaly, and sometimes assume the form of minute irregular prisms. It is then thrown on a filter, and edulcorated with cold water till the sulphate of soda and excess of sulphuric acid are entirely removed.

Boracic acid in this state is a hydrate. Its precise degree of solubility in water has not been determined with accuracy; but it is much more soluble in hot than in cold water. Boiling alcohol dissolves it freely, and the solution, when set on fire, burns with a beautiful green flame; a test which affords the surest indication of the presence of boracic acid. Its specific gravity is 1.479. It has no odour, and its taste is rather bitter than acid. It reddens litmus paper feebly, and effervesces with alkaline carbonates. From the weakness of its acid pro-

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\* *Recherches Physico-Chimiques*, vol. i.

perties, all the borates, when in solution, are decomposed by the stronger acids.

When hydrous boracic acid is exposed to a gradually increasing heat in a platinum crucible, its water of crystallization is wholly expelled, and a fused mass remains which bears a white heat without volatilizing. On cooling, it forms a hard, colourless, transparent glass, which is anhydrous boracic acid. If the water of crystallization be driven off by the sudden application of a strong heat, a large quantity of boracic acid is carried away during the rapid escape of watery vapour. The same happens, though in a less degree, when a solution of boracic acid in water is boiled briskly. Vitrified boracic acid should be preserved in well stopped vessels; for if exposed to the air, it absorbs water, and gradually loses its transparency. Its specific gravity is 1.803. It is exceedingly fusible, and communicates this property to the substances with which it unites. For this reason borax is often used as a flux.

The most obvious mode of determining the composition of boracic acid is to burn a known quantity of boron, and ascertain its increase of weight when the combustion ceases. This method, however, though apparently simple, is very difficult of execution; for the boracic acid fuses at the moment of being generated, and by glazing the surface of the unconsumed boron, protects it from oxidation. Hence it was that the experiments performed by Gay-Lussac and Thénard on this subject, led to results widely different from those which Sir H. Davy obtained by a similar process. Dr Thomson, from data furnished partly by himself, and partly by Sir H. Davy, infers that the atomic weight of boron is 8, and that boracic acid is composed of

Boron	.	.	8, or one atom.
Oxygen	.	.	16, or two atoms.

Consequently, the combining proportion of boracic acid is 24.

Crystallized boracic acid, according to the same chemist, is composed of

Boracic acid	.	.	24, or one atom.
Water	.	.	18, or two atoms.

and therefore its atomic weight is . 42.

## SECTION X.

### SELENIUM.

Selenium has hitherto been found in very small quantity. It occurs for the most part in combination with sulphur in some kinds of iron pyrites. Stromeyer has also detected it, as a sulphuret of selenium, among the volcanic products of the Lipari isles. It is found likewise at Clausthal, in the Hartz mountains, combined, according to Stromeyer and Rose, with several metals, such as lead, cobalt, silver, mercury, and copper. It was discovered in 1818 by Berzelius in the sulphur obtained by sublimation from the iron pyrites of Fahlun. In a

manufactory of sulphuric acid at which this sulphur was employed, it was observed that a reddish-coloured matter always collected at the bottom of the leaden chamber; and, on burning this substance, Berzelius perceived a strong and peculiar odour, similar to that of decayed horse-radish, which induced him to submit it to a careful examination, and thus led to the discovery of selenium\*.

Selenium, at common temperatures, is a brittle opaque solid body, without taste or odour. It has a metallic lustre and the aspect of lead, when in mass; but is of a deep red colour when reduced to powder. Its specific gravity is between 4.3 and 4.32. At 212° Fahrenheit it softens, and is then so tenacious that it may be drawn out into fine threads which are transparent, and appear red by transmitted light. It becomes quite fluid at a temperature somewhat above that of boiling water. It boils at about 650° Fahrenheit, forming a vapour which has a deep yellow colour, but emitting no odour. It may be sublimed in close vessels without change, and condenses again into dark globules of a metallic lustre, or as a cinnabar red powder, according as the space in which it collects is small or large. Berzelius at first regarded it as a metal; but, since it is a bad conductor of caloric and electricity, it more properly belongs to the class of the simple non-metallic bodies.

Selenium is insoluble in water. It suffers no change from mere exposure to the atmosphere; but if heated in the open air, it combines readily with oxygen, and two compounds, the oxide and acid of selenium, are generated. If the experiment is made by throwing upon it the oxidizing part of the blow-pipe flame, it tinges the flame of a light-blue colour, and exhales so strong an odour of decayed horse-radish, that 1-50th of a grain is said to be sufficient to scent the air of a large apartment. By this character the presence of selenium whether alone or in combination may always be detected.

*Oxide of Selenium.*—This compound is formed in greatest abundance by heating selenium in a limited quantity of atmospheric air, and washing the product to separate the selenic acid. It is a colourless gas, which is very sparingly soluble in water, and does not possess any acid properties. It is the cause of the peculiar odour which is emitted during the oxidation of selenium. Its composition has not been determined, but it probably contains an atom of each of its elements.

*Selenic Acid.*—Selenic acid is most conveniently prepared by digesting selenium in nitric or nitro-muriatic acid till it is completely dissolved. On evaporating the solution to dryness, a white residue is left, which is selenic acid. By an increase of temperature, the acid itself sublimes, and condenses again unchanged into long four-sided needles. It attracts moisture from the air, whereby it suffers an imperfect liquefaction. It dissolves in alcohol and water. It has distinct acid properties, and its salts are called seleniates.

Selenic acid is readily decomposed by all substances which have a strong affinity for oxygen, such as the sulphurous and phosphorous acids. When sulphurous acid, or an alkaline sulphite, is added to a solution of selenic acid, a red coloured powder, pure selenium, is thrown down, and the sulphurous passes into the sulphuric acid.

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\* An. de Ch. et de Phys. vol. ix. or Annals of Philosophy, vol. 13.



Sulphuretted hydrogen also decomposes it; and an orange-yellow precipitate subsides, which is a sulphuret of selenium.

The atomic weight of selenium, deduced chiefly from the experiments of Berzelius, is 40; and the selenic acid, according to the analysis of the same chemist, consists of

Selenium	.	40	.	one atom.
Oxygen	.	16	.	two atoms.
		—		
		56		

## SECTION XI.

### CHLORINE.

The discovery of chlorine was made in 1770 by Scheele while investigating the nature of manganese, and he described it under the name of *dephlogisticated marine acid*. The French chemists called it *oxygenized muriatic acid*, a term which was afterwards contracted to *oxymuriatic acid*, from an opinion proposed by Berthollet that it is a compound of muriatic acid and oxygen. In 1809 Gay-Lussac and Thénard published an abstract of some experiments upon the subject, which subsequently appeared at length in their *Recherches Physico-Chimiques*, wherein they state that oxymuriatic acid might be regarded as a simple body, though they gave the preference to the doctrine advanced by Berthollet. Sir H. Davy engaged in the inquiry about the same time, and after having exposed oxymuriatic acid to the most powerful decomposing agents which chemists possess, without being able to effect its decomposition, he communicated to the Royal Society a paper in which he denied its compound nature and maintained that, according to the true logic of chemistry, it is entitled to rank with simple bodies. This view, which is commonly termed the *new theory of chlorine*, though strongly objected to at the time it was first proposed, is now almost universally received by chemists, and accordingly is adopted in this work. The grounds of preference will hereafter be briefly stated.

Chlorine gas is obtained by the action of muriatic acid on the peroxide of manganese. The most convenient method of preparing it is by mixing concentrated muriatic acid, contained in a glass flask, with half its weight of finely powdered peroxide of manganese. An effervescence, owing to the escape of chlorine, takes place even in the cold; but the gas is evolved much more freely by the application of a moderate heat. It should be collected in inverted glass bottles filled with warm water; and when the water is wholly displaced by the gas, the bottles should be closed with a well-ground glass stopper.

Before explaining the theory of this process, it may be premised that muriatic acid consists of 36 parts or one atom of chlorine, and 1 part or one atom of hydrogen. The peroxide of manganese, as already mentioned (page 110,) is composed of 28 or one atom of manganese, and 16 or two atoms of oxygen. When these compounds react on one another, one atom of each is decomposed. The peroxide of manganese gives one atom of oxygen to the hydrogen of the inuria-

tic acid, in consequence of which one atom of water is generated, and one atom of chlorine disengaged; while the protoxide of manganese unites with an atom of undecomposed muriatic acid, and forms an atom of the muriate of the protoxide of manganese. Consequently, for every 44 grains of the peroxide of manganese, 74 ( $37 \times 2$ ) grains of muriatic acid disappear; and 36 chlorine, 9 water, and 73 protomuriate of manganese, are the products of the decomposition. The affinities which determine these changes are the attraction of oxygen for hydrogen, and of the protoxide of manganese for muriatic acid.

When it is an object to prepare chlorine at the cheapest rate, as for the purposes of manufacture, the preceding process is modified in the following manner. Three parts of sea-salt are intimately mixed with one of the peroxide of manganese, and to this mixture two parts of sulphuric acid, diluted with an equal weight of water, are then added. By the action of sulphuric acid on sea-salt muriatic acid is disengaged, which reacts as in the former case upon the peroxide of manganese; so that, instead of adding muriatic acid directly to the manganese, the materials for forming it are employed.

Chlorine\* is a yellowish-green coloured gas, which has an astringent taste, and a disagreeable odour. It is one of the most suffocating of the gases, exciting spasm and great irritation of the glottis, even when considerably diluted with air. When strongly and suddenly compressed, it emits both heat and light, a character which it possesses in common with oxygen gas. According to Sir H. Davy, 100 cubic inches of it at  $60^{\circ}$  F., and when the barometer stands at 30 inches, weigh between 76 and 77 grains. Dr Thomson states its weight at 76.25 grains, and his result agrees very nearly with that of Gay-Lussac and Thénard. Adopting this estimate, its specific gravity is 2.5. Under the pressure of about four atmospheres it is a limpid liquid of a bright yellow colour, which does not freeze at the temperature of zero, and which assumes the gaseous form with the appearance of ebullition when the pressure is removed.

Cold recently boiled water, at the common pressure, absorbs twice its volume of chlorine, and yields it again when heated. The solution, which is made by passing a current of chlorine gas through cold water, has the colour, taste, and most of the other properties of the gas itself. When moist chlorine gas is exposed to a cold of  $32^{\circ}$  F., yellow crystals are formed, which consist of water and chlorine in definite proportions. They are composed, according to Mr Faraday, of 36 or one atom of chlorine to 90 or ten atoms of water.

Chlorine experiences no chemical change from the action of the imponderables. Thus it is not affected chemically by intense heat, by strong shocks of electricity, or by a powerful galvanic battery. Sir H. Davy exposed it also to the action of charcoal heated to whiteness by galvanic electricity, without separating oxygen from it, or in any way affecting its nature. Light does not act on dry chlorine; but if water be present, the chlorine decomposes that liquid, unites with the hydrogen to form muriatic acid, and oxygen gas is set at liberty. This change takes place quickly in sunshine, more slowly in diffused daylight, and not at all when the light is wholly excluded. Hence the necessity of keeping moist chlorine gas, or its solution, in a dark place, if it is wished to preserve it for any time.

\* From *χλαρος*, green.

Chlorine is a supporter of combustion. If a lighted taper be plunged into chlorine gas, it burns with a small red flame, and emits a large quantity of smoke. Phosphorus takes fire in it spontaneously, and burns with a pale white light. Several of the metals, such as tin, copper, arsenic, antimony, and zinc, when introduced into chlorine in the state of powder or in fine leaves, are suddenly inflamed. In all these cases the combustible substances unite with chlorine.

Chlorine has a very powerful attraction for hydrogen; and many of the chemical phenomena to which chlorine gives rise, are owing to this property. A striking example is its power of decomposing water by the action of light, or at a red heat; and most compound substances, of which hydrogen is an element, are deprived of that principle, and therefore decomposed in like manner. For the same reason, when chlorine, water, and some other body, which has a strong affinity for oxygen, are presented to one another, the water is resolved into its elements, the hydrogen attaches itself to the chlorine, and the oxygen to the other body. Hence it happens that chlorine is indirectly one of the most powerful oxidizing agents which we possess.

When any compound of chlorine and an inflammable is exposed to the influence of galvanism, the inflammable body goes over to the negative, and the chlorine to the positive pole of the battery. This establishes a close analogy between oxygen and chlorine, both of them being supporters of combustion, and both negative electrics.

Chlorine, though formerly called an acid, possesses no acid properties. It has not a sour taste, does not redden the blue colour of plants, and shows little disposition to unite with alkalis. Its strong affinity for the metals is sufficient to prove that it is not an acid; for chemists are not acquainted with any instance of direct combination between an acid and a metal.

The mutual action of chlorine and the pure alkalis leads to complicated changes. If chlorine gas is passed into a solution of potash till all alkaline reaction ceases, a liquid is obtained which has the odour of a solution of chlorine in water. But on applying heat, the chlorine disappears entirely, and the solution is found to contain two neutral salts, the chlorate and muriate of potash. The production of the two acids is owing to the decomposition of water, the elements of which unite with separate portions of chlorine, and form the chloric and muriatic acids. The affinities which give rise to this change, are the attraction of chlorine for hydrogen, of chlorine for oxygen, and of the two resulting acids for the alkali.

One of the most important properties of chlorine is its bleaching power. All animal and vegetable colours are speedily removed by chlorine; and when the colour is once discharged, it can never be restored. Sir H. Davy proved that chlorine cannot bleach unless water is present. Thus, dry litmus paper suffers no change in dry chlorine; but when water is admitted, the colour speedily disappears. It is well known also, that muriatic acid is always generated when chlorine bleaches. From these facts it is inferred that water is decomposed during the process; that its hydrogen unites with chlorine; and that the decomposition of the colouring matter is occasioned by the oxygen which is liberated. The bleaching property of the deutoxide of hydrogen, of which oxygen is certainly the decolorizing principle, leaves little doubt of the accuracy of the foregoing explanation.

Chlorine is useful, likewise, for the purposes of fumigation. The experience of Guyton-Morveau is sufficient evidence of its power in

destroying the volatile principles given off by putrescying animal matter; and it probably acts in a similar way on contagious effluvia.

Chlorine is in general easily recognised by its colour and odour. Chemically it may be detected by its bleaching property, added to the circumstance that a solution of the nitrate of silver occasions in it a dense white precipitate (a compound of chlorine and metallic silver), which becomes dark on exposure to light, is insoluble in acids, and dissolves completely in pure ammonia.

The compounds of chlorine, which are not acid, are termed *chlorides* or *chlorurets*. The former expression is perhaps the more appropriate, from the analogy between chlorine and oxygen.

### *Compound of Chlorine and Hydrogen.—Muriatic Acid Gas\*.*

*Muriatic or hydrochloric acid gas* was discovered by Priestley in 1772. It may be conveniently prepared by putting an ounce of the strong muriatic acid of the pharmacopœia into a glass flask, and heating it by means of a lamp till the liquid boils. Pure muriatic acid gas is freely evolved, and may be collected over mercury. Another method of preparing it is by the action of concentrated sulphuric acid on an equal weight of sea-salt. A brisk effervescence ensues at the moment of making the mixture, and on the application of heat a large quantity of muriatic acid gas is disengaged. In the first process, muriatic acid, previously dissolved in water, is simply expelled from the solution by an increased temperature. The explanation of the second process is rather more complicated. Sea-salt was formerly supposed to be a compound of muriatic acid and soda; and, on this supposition, the soda was believed merely to quit the muriatic and unite with the sulphuric acid. But, according to the experiments of Gay-Lussac and Thénard and Sir H. Davy, sea-salt in its dry state consists, not of muriatic acid and soda, but of chlorine and sodium, the metallic base of soda. The proportions of its constituents are

Chlorine	36	.	1 atom,
Sodium	24	.	1 atom.

When sulphuric acid is added to it, one atom of water is resolved into its elements; the hydrogen unites with chlorine, forming muriatic acid, which escapes in the form of gas; while soda is generated by the combination of the oxygen with sodium, which combines with the sulphuric acid, and forms sulphate of soda. The water contained in the liquid sulphuric acid is therefore essential to the success of the operation. The affinities which determine the change are the attraction of chlorine for hydrogen, of sodium for oxygen, and of soda for sulphuric acid.

Muriatic acid may be generated by the direct union of its elements. When equal measures of chlorine and hydrogen are mixed together, and an electric spark is passed through the mixture, instantaneous combination takes place, heat and light are emitted, and muriatic acid

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\* I have here deviated slightly from my arrangement. I have done so, because it will facilitate the study of the compounds of chlorine with the simple non-metallic bodies, to describe them in the same section. Iodine, for a like reason, will be treated in a similar manner.

is generated. A similar effect is produced by flame, by a red-hot body, and by spongy platinum. Light also causes them to unite. A mixture of the two gases may be preserved without change in a dark place: but if exposed to the diffused light of day, a gradual combination ensues, and is completed in the course of 24 hours. The direct solar rays produce, like flame or electricity, a sudden inflammation of the whole mixture, accompanied with an explosion; and, according to Mr Brande, the vivid light emitted by charcoal intensely heated by galvanic electricity acts in a similar manner.

The experiments of Davy and Gay-Lussac and Thénard concur in proving that hydrogen and chlorine unite in equal volumes, and that the muriatic acid, which is the sole and constant product, occupies the same space as the gases from which it is formed. From these facts the composition of muriatic acid is easily inferred. For, as

	<i>Grains.</i>
50 Cubic inches of Chlorine weigh . . .	38.125
and 50 Hydrogen . . .	1.059

100 Cubic inches of Muriatic acid gas must weigh	39.184
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Its specific gravity, therefore, is 1.2847. By weight it consists of

Chlorine . . .	38.125	36
Hydrogen . . .	1.059	1

Since chlorine and hydrogen unite in one proportion only, chemists regard muriatic acid as a compound of one atom of each of its elements, a conclusion which is fully justified by the proportions in which chlorine and hydrogen unite with other bodies. Hence, 36 is the weight of one atom of chlorine, and 37 of muriatic acid.

Muriatic acid is a colourless gas, of a pungent odour, and acid taste. Under a pressure of 40 atmospheres, and at the temperature of 50° F. it is liquid. It is quite irrespirable, exciting violent spasm of the glottis; but when diluted with air, it is far less irritating than chlorine. All burning bodies are extinguished by it, and the gas itself does not take fire on the approach of flame.

Muriatic acid gas is not chemically changed by mere heat. It is readily decomposed by galvanism, hydrogen appearing at the negative, and chlorine at the positive pole. It is also decomposed by ordinary electricity. The decomposition, however, is incomplete; for though one electric spark resolves a portion of the gas into its elements, the next shock in a great measure effects their reunion. It is not affected by oxygen under common circumstances; but if a mixture of oxygen and muriatic acid gases is electrified, the oxygen unites with the hydrogen of the muriatic acid to form water, and chlorine is set at liberty. For this and the preceding fact we are indebted to the researches of Dr Henry.

One of the most striking properties of muriatic acid gas is its powerful attraction for water. A dense white cloud appears whenever muriatic acid escapes into the air, owing to a combination which takes place between the acid and watery vapour. When a piece of ice is put into a jar full of the gas confined over mercury, the ice liquefies on the instant, and the whole of the gas disappears in the course of a few seconds. On opening a long wide jar of muriatic acid gas under water, the absorption of the gas takes place so instantaneously, that



the water is forced up into the jar with the same violence as into a vacuum.

A concentrated solution of muriatic acid gas in water has long been known under the names of *spirit of salt*, and of *marine* or *muriatic acid*. It is made by passing a current of gas into water as long as any of it is absorbed. A considerable increase of temperature takes place during the absorption, and therefore the apparatus should be kept cool by ice. Sir H. Davy states (*Elements*, p. 252.) that water at the temperature of 40° F. absorbs 480 times its volume of the gas, and that the solution has a density of 1.2109. Dr Thomson finds that one cubic inch of water at 69° F. absorbs 418 cubic inches of gas, and occupies the space of 1.34 cubic inch. The solution has a density of 1.1958, and one cubic inch of it contains 311.04 cubic inches of muriatic acid gas. The quantity of real acid contained in solutions of different densities may be determined by ascertaining the quantity of pure marble dissolved by a given weight of each. Every 50 grains of marble correspond to 37 of real acid. The following table from Dr Thomson's "*Principles of Chemistry*," is constructed by this rule. The first and second columns show the atomic constitution of each acid.

*Table exhibiting the specific gravity of Muriatic Acid of determinate strengths.*

<i>Atoms of Acid.</i>	<i>Atoms of water.</i>	<i>Real acid in 100 of the liquid.</i>	<i>Specific Gravity.</i>
1	6	40.659	1.203
1	7	37.000	1.179
1	8	33.945	1.162
1	9	31.346	1.149
1	10	29.134	1.139
1	11	27.206	1.1285
1	12	25.517	1.1197
1	13	24.026	1.1127
1	14	22.700	1.1060
1	15	21.512	1.1008
1	16	20.442	1.0960
1	17	19.474	1.0902
1	18	18.590	1.0860
1	19	17.790	1.0820
1	20	17.051	1.0780

All the Pharmacopœias give directions for forming muriatic acid. The process recommended by the Edinburgh College is practically good. The proportions they recommend are equal weights of sea-salt, water, and sulphuric acid, more acid being purposely employed than is sufficient to form a neutral sulphate with the soda, so that the more perfect decomposition of the sea salt may be insured. The acid, to prevent too violent an effervescence at first, is mixed with one-third of the water, and when the mixture has cooled, it is poured upon the salt previously introduced into a glass retort. The distillation is continued to dryness; and the gas, as it escapes, is conducted into the remainder of the water. The theory of the process has already been explained. The residue is a mixture of the sulphate and bi-sulphate

of soda. The specific gravity of muriatic acid obtained by this process, is 1.170.

The common muriatic acid of commerce has a yellow colour, and is always impure. The usual impurities are nitric acid, sulphuric acid, and oxide of iron. The presence of nitric acid may be inferred if the muriatic acid has the property of dissolving gold leaf. Iron may be detected by the ferrocyanate of potassa, and the sulphuric acid by muriate of baryta, the suspected muriatic acid being previously diluted with three or four parts of water. To provide against the presence of nitric acid, the sea-salt is first ignited, as recommended by the Edinburgh College, to decompose any nitre which it may contain. The other impurities may be avoided by employing a Woulfe's Apparatus. A few drachms of water are put into the first bottle, to retain the muriate of iron and sulphuric acid which pass over, and the muriatic acid gas is condensed in the second.

Pure concentrated muriatic acid is a colourless liquid, which emits white vapours when exposed to the air, is intensely sour, reddens litmus paper strongly, and unites with alkalis. It combines with water in every proportion, and causes an increase of temperature when mixed with it, though in a much less degree than sulphuric acid. It freezes at  $-60^{\circ}$  F.; and boils at  $110^{\circ}$  F., or a little higher, giving off pure muriatic acid gas in large quantity.

Muriatic acid is decomposed by substances which yield oxygen readily. Thus several peroxides, such as those of manganese, cobalt, and lead, effect its decomposition. Chloric and iodic acids act on the same principle. The action of nitric acid is illustrative of the same circumstance. A mixture of nitric and muriatic acids, in the proportion of one measure of the former to two of the latter, has long been known under the name of *Aqua regia* as a solvent for gold and platinum. When these acids are mixed together, the solution instantly becomes yellow; and on heating the mixture, pure chlorine is evolved, and the colour of the solution deepens. On continuing the heat, chlorine and nitrous acid vapours are disengaged. At length the evolution of chlorine ceases, and the residual liquid is found to be a solution of muriatic and nitrous acids, which is incapable of dissolving gold. The explanation of these facts is, (Sir H. Davy in the Quarterly Journal, vol. i.) that nitric and muriatic acids decompose one another, giving rise to the production of water and nitrous acid, and the separation of chlorine; while muriatic and nitrous acids may be heated together without mutual decomposition. It is hence inferred that the power of nitro-muriatic acid in dissolving gold is owing to the chlorine which is liberated.

Muriatic acid is readily distinguished by its odour, by acting on a solution of the nitrate of silver in the same manner as chlorine, and by the absence of bleaching properties.

### *Compounds of Chlorine and Oxygen.*

Chlorine unites with oxygen in four different proportions. The leading character of these compounds is derived from the circumstance that chlorine and oxygen, the attraction of which for most elementary substances is so energetic, have but a feeble affinity for one another. These principles, consequently, are never met with in nature in a state of combination. Indeed, they cannot be made to combine directly; and when they do unite, very slight causes effect their sepa-

ration. Notwithstanding this, their union is always regulated by the law of definite proportions, as appears from the following tabular view of the constitution of the compounds to which they give rise\*.

	Chlorine.	Oxygen.
Protoxide of Chlorine	36	8
Peroxide of Chlorine	36	32
Chloric acid	36	40
Perchloric acid	36	56

*Protoxide of Chlorine.*—This gas was discovered in 1811, by Sir H. Davy, and was described by him in the Philosophical Transactions for that year under the name of *Euchlorine*. It is made by the action of muriatic acid on the chlorate of potassa; and its production is explicable on the fact, that muriatic and chloric acids mutually decompose each other. When muriatic acid and chlorate of potassa are mixed together, a part of the muriatic acid unites with the potassa of the salt, and thus sets chloric acid free, which instantly reacts on the free muriatic acid. The result of the reaction depends on the manner in which the operation is conducted. If the chlorate of potassa is mixed with an excess of concentrated muriatic acid, the chloric acid undergoes complete decomposition. For one atom of the chloric, five atoms of muriatic acid are decomposed: the five atoms of oxygen contained in the former unite with the hydrogen of the latter, producing five atoms of water; while the chlorine of both acids is disengaged. If, on the contrary, the salt is in excess, and the muriatic acid diluted, the chloric acid is deprived of a part of its oxygen only; and the products are water, protoxide of chlorine, and chlorine, the two latter escaping in the gaseous form. From the proportion of these gases, I apprehend that for each atom of the chloric, three of muriatic acid must be decomposed; and that by the reaction of their elements, they yield three atoms of water, two of pure chlorine, and two of the protoxide of chlorine.

The best proportion of the ingredients for forming this compound is two parts of the chlorate of potassa, one of strong muriatic acid, and one of water. Effervescence ensues on the application of a gentle heat, and the gases should be collected over mercury. The chlorine combines with the mercury, and the protoxide of chlorine is left.

The protoxide of chlorine has a yellowish-green colour similar to that of chlorine, but considerably more brilliant, which induced Sir H. Davy to give it the name of *euchlorine*. Its odour is like that of burned sugar. Water dissolves eight or ten times its volume of the gas, and acquires a colour approaching to orange. It bleaches vegetable substances, but gives the blue colours a tint of red before destroying them. It does not unite with alkalies, and therefore is not an acid.

The protoxide of chlorine is explosive in a high degree. The heat of the hand, or the pressure occasioned in transferring it from one vessel to another, sometimes causes an explosion. This effect is also occasioned by phosphorus, which bursts into flame at the moment of immersion. All burning bodies, by their heat, occasion an explosion, and then burn vividly in the decomposed gas. With hydrogen it forms a mixture which explodes by flame or the electric spark, with

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\* Note by Gay-Lussac in the 9th volume of the *An. de Ch. et de Physique*.

production of water and muriatic acid. The best proportion is 50 measures of the protoxide of chlorine to 80 of hydrogen.

The protoxide of chlorine is easily analyzed by heating a known quantity of it in a strong tube over mercury. An explosion takes place; and 50 of the gas expand to 60 measures, 20 of which are oxygen, and 40 chlorine. The specific gravity of a gas so constituted must be 2.444, and its composition by weight is, chlorine 36 + oxygen 8. The weight of its atom is consequently 44.

*Peroxide of Chlorine.*—The peroxide of chlorine was discovered in 1815 by Sir H. Davy\*, and soon after by Count Stadion of Vienna. It is formed by the action of sulphuric acid on the chlorate of potassa. A quantity of this salt, not exceeding 50 or 60 grains, is reduced to powder, and made into a paste by the addition of strong sulphuric acid. The mixture, which acquires a deep yellow colour, is placed in a glass retort, and is heated by warm water, the temperature of which is kept under 212° F. A bright yellowish-green gas of a still richer colour than the protoxide of chlorine is disengaged, which has an aromatic odour without any smell of chlorine, is absorbed rapidly by water, to which it communicates its tint, and has no sensible action on mercury. This gas is the peroxide of chlorine.

The chemical changes which take place in the process are explained in the following manner. The sulphuric acid decomposes some of the chlorate of potassa, and sets chloric acid at liberty. The chloric acid, at the moment of separation, resolves itself into peroxide of chlorine and oxygen; the last of which, instead of escaping as free oxygen gas, goes over to the acid of some undecomposed chlorate of potassa, and converts it into perchloric acid. The whole products are bisulphate and perchlorate of potassa, and peroxide of chlorine. It is most probable, from the data contained in the preceding table, that every three atoms of chloric acid yield one atom of the perchloric acid and two atoms of the peroxide of chlorine.

The peroxide of chlorine does not unite with alkalis. It destroys most vegetable blue colours without previously reddening them. Phosphorus takes fire when introduced into it, and occasions an explosion. It explodes violently when heated to a temperature of 212° F., emits a strong light, and undergoes a greater expansion than the protoxide of chlorine. According to Sir H. Davy, whose result is confirmed by Gay-Lussac, 40 measures of the gas occupy the space of 60 measures after the explosion; and of these, 20 are chlorine and 40 oxygen. The peroxide is therefore composed of 36, or one atom of chlorine united with 32 or four atoms of oxygen. Its specific gravity must be 2.361.

*Chloric acid.*—When to a dilute solution of the chlorate of baryta a quantity of weak sulphuric acid, exactly sufficient for combining with the baryta, is added, the insoluble sulphate of baryta subsides, and pure chloric acid remains in the liquid. This acid, the existence of which was originally observed by Mr Chenevix, was first obtained in a separate state by Gay-Lussac.

Chloric acid reddens vegetable blue colour, has a sour taste, and forms neutral salts, called *chlorates*, (formerly *hyperoxymuriates*) with alkaline bases. It possesses no bleaching properties, a circumstance by which it is distinguished from chlorine. It gives no preci-

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\* Philosophical Transactions for 1815.

pitate in solution of nitrate of silver, and hence cannot be mistaken for muriatic acid. Its solution may be concentrated by a gentle heat till it acquires an oily consistence without decomposition; but at a higher temperature, the acid in part is volatilized unchanged, while another portion is converted into chlorine and oxygen. It is easily decomposed by deoxidizing agents. Sulphurous acid, for instance, deprives it of oxygen, with formation of sulphuric acid and evolution of chlorine. By the action of sulphuretted hydrogen, water is generated, while sulphur and chlorine are set free. The power of muriatic acid in effecting its decomposition has already been explained.

Chloric acid is readily known by forming a salt with potassa, which crystallizes in tables, and has a pearly lustre, which deflagrates like nitre when flung on burning charcoal, and yields the peroxide of chlorine by the action of concentrated sulphuric acid. The chlorate of potassa, like most of the chlorates, gives off pure oxygen when heated to redness, and leaves a residue of the chloride of potassium. This was the mode by which Gay-Lussac ascertained the composition of chloric acid, as stated in the table. (*Annales de Chimie*, vol. xci.)

*Perchloric acid*.—The saline matter which remains in the retort after forming the peroxide of chlorine, is a mixture of the perchlorate and bisulphate of potassa, and by washing it with cold water, the bisulphate is dissolved, and the perchlorate is left. The perchloric acid may be prepared from this salt by mixing it in a retort with half its weight of sulphuric acid, diluted with one-third of water, and applying heat to the mixture. At the temperature of about 284° F. white vapours rise, which condense as a colourless liquid in the receiver. This is a solution of the perchloric acid.

The properties of the perchloric acid have hitherto been little examined. Count Stadion\*, its discoverer, found it to be a compound of one atom or 36 of chlorine to 56 or seven atoms of oxygen; and his analysis has been confirmed by Gay-Lussac†.

### *Chloride of Nitrogen.*

The mutual affinity of chlorine and nitrogen is very slight; they do not combine at all if presented to each other in their gaseous form; and when combined, they are easily separated. The chloride of nitrogen is formed by the action of chlorine on some salt of ammonia. Its formation is owing to the decomposition of ammonia (a compound of hydrogen and nitrogen) by chlorine. The hydrogen of the ammonia unites with chlorine, and forms muriatic acid; while the nitrogen of the ammonia, being presented in its nascent state to chlorine, dissolved in the solution, enters into combination with it.

A convenient method of preparing the chloride of nitrogen is the following. An ounce of muriate of ammonia is dissolved in twelve or sixteen ounces of hot water; and when the solution has cooled to the temperature of 90° F., a glass bottle, with a wide mouth, full of chlorine, is inverted in it. The solution gradually absorbs the chlorine, and acquires a yellow colour; and in about twenty minutes, or half an hour, minute globules of a yellow fluid are seen floating like oil upon its surface, which, after acquiring the size of a small pea, sink to the bottom of the liquid. The drops of the chloride of nitrogen, as they

\* *Annales de Ch. et de Physique*, vol. viii.

† *Ibid.* vol. ix.



descend, should be collected in a small saucer of lead, placed for that purpose under the mouth of the bottle.

The chloride of nitrogen, discovered in 1811 by M. Dulong, (*An. de Chimie*, vol. lxxxvi.) is one of the most explosive compounds yet known, having been the cause of serious accidents both to its discoverer and to Sir H. Davy\*. Its specific gravity is 1.653. It does not congeal by the intense cold produced by a mixture of snow and salt. It may be distilled at 160° F.; but at a temperature between 200° and 212° F. it explodes. It appears from the investigation of Messrs Porrett, Wilson, and Kirk†, that mere contact with some substances of a combustible nature causes detonation even at common temperatures. This property belongs particularly to the oils, both volatile and fixed. I have never known olive oil fail in producing the effect. The products of the explosion are chlorine and nitrogen.

Sir H. Davy analyzed the chloride of nitrogen by means of mercury, which unites with the chlorine, and liberates the nitrogen. He inferred from his analysis that its elements are united in the proportion of four measures of chlorine to one nitrogen; and it hence follows that, by weight, it consists of

Chlorine	.	144	.	.	or four atoms.
Nitrogen	.	14	.	.	or one atom.

### *Compounds of Chlorine and Carbon.—Perchloride of Carbon.*

For the knowledge of the compounds of chlorine and carbon, chemists are indebted to the ingenuity of Mr Faraday. When olefiant gas (a compound of carbon and hydrogen) is mixed with chlorine, combination takes place between them, and an oily-like liquid is generated, which consists of chlorine, carbon, and hydrogen. On exposing this liquid in a vessel full of chlorine gas to the direct solar rays, the chlorine acts upon and decomposes the liquid, muriatic acid is set free, and the carbon, at the moment of separation, unites with chlorine‡.

The *perchloride of carbon*, as this compound is named by Mr Faraday, is solid at common temperatures, has an aromatic odour approaching to that of camphor, is a non-conductor of electricity, and refracts light very powerfully. Its specific gravity is exactly double that of water. It fuses at 320° F., and after fusion it is colourless and very transparent. It boils at 360° F., and may be distilled without change, assuming a crystalline arrangement as it condenses. It is sparingly soluble in water, but dissolves in alcohol and ether, especially by the aid of heat. It is soluble also in fixed and volatile oils.

The perchloride of carbon burns with a red light when held in the flame of a spirit-lamp, giving out acid vapours and smoke; but the combustion ceases as soon as it is withdrawn. It burns vividly in oxygen gas. Alkalies do not act upon it; nor is it changed by the

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\* Philosophical Transactions, 1813.

† Nicholson's Journal, vol. xxxiv.

‡ The reader will find the details of this process in the Philosophical Transactions for 1821, or in the second volume, N. S. of the Annals of Philosophy.

stronger acids, such as the muriatic, nitric, or sulphuric acids, even with the aid of heat; charcoal is separated, and muriatic acid gas is evolved. On passing its vapour over the peroxides of metals, such as those of mercury and copper, heated to redness, a chloride of the metal and carbonic acid are generated. Protoxides, under the same treatment, yield carbonic oxide gas and a metallic chloride. Most of the metals decompose it also at the temperature of ignition, uniting with the chlorine, and causing a deposition of charcoal.

From the proportions of chlorine and olefiant gas employed in forming the perchloride of carbon, and from its analysis, made by passing it over the peroxide of copper at the temperature of ignition, Mr Faraday infers that this compound consists of

Chlorine	.	108	.	.	or three atoms.
Carbon	.	12	.	.	or two atoms.

*Protochloride of carbon.*—When the vapour of the perchloride of carbon is passed through a red-hot glass or porcelain tube, containing fragments of rock crystal to increase the extent of heated surface, a partial decomposition takes place; chlorine gas escapes, and a fluid passes over which Mr Faraday calls the *protochloride of carbon*.

The protochloride of carbon is a limpid colourless fluid, which does not congeal at zero of Fahrenheit, and at 160° or 170° F. is converted into vapour. It may be distilled repeatedly without change; but when exposed to a red heat some of it is resolved into its elements. Its specific gravity is 1.5526. In its chemical relations it is very analogous to the perchloride of carbon. Mr Faraday analyzed it by passing its vapour over ignited peroxide of copper, and infers from the products of its decomposition—carbonic acid and chloride of copper—that it is composed of,

Chlorine	.	36	.	.	or one atom,
Carbon	.	6	.	.	or one atom.

A third compound of chlorine and carbon is described in the first volume, New Series, of the Annals of Philosophy. It was brought from Sweden by M. Julin, and is said to have been formed during the distillation of nitric acid from crude nitre, and sulphate of iron. It occurs in small, soft, adhesive fibres of a white colour, which have a peculiar odour, somewhat resembling spermaceti. It fuses on the application of heat, and boils at a temperature between 350° and 450° F. At 250° F. it sublimes slowly, and condenses again in the form of long needles. It is insoluble in water, acids, and alkalies; but is dissolved by hot oil of turpentine or by alcohol, and forms acicular crystals as the solution cools. It burns with a red flame, emitting much smoke, and fumes of muriatic acid gas.

The nature of this substance is shown by the following circumstances. When its vapour is exposed to a red heat, an evolution of chlorine gas ensues, and charcoal is deposited. A similar deposition of charcoal is produced by heating it with phosphorus, iron, or tin, and a chloride is formed at the same time. Potassium burns vividly in its vapour, with formation of the chloride of potassium, and separation of charcoal. On detonating a mixture of its vapour with oxygen gas over mercury a chloride of that metal and carbonic acid are generated. From these facts, the greater part of which were ascer-

tained by Messrs Phillips and Faraday\*, it follows that the substance brought from Sweden by M. Julin is a compound of chlorine and carbon; and the same able chemists conclude from their analysis that its elements are united in the proportion of

Chlorine	.	36, or one atom.
Carbon	.	12, or two atoms.

### *Chloride of Sulphur.*

The *Chloride of Sulphur* was discovered in 1804, by Dr Thomson†, and was afterwards examined by Berthollet‡. It is most conveniently prepared by passing a current of chlorine gas over flowers of sulphur gently heated. Direct combination takes place, and the product is obtained under the form of a liquid which appears red by reflected, and yellowish-green by transmitted light. Its density is 1.6. It is volatile below 200° F. and condenses again without change in cooling. It emits acrid fumes when exposed to the air, which irritate the eyes powerfully, and have an odour somewhat resembling sea-weed, but much stronger. Dry litmus paper is not reddened by it, nor does it unite with alkalies. It acts with energy on water;—mutual decomposition ensues, the water becomes cloudy from deposition of sulphur, and a solution is obtained, in which muriatic, sulphurous, and sulphuric acids may be detected. Similar phenomena ensue when it is mixed with alcohol or ether.

Sir H. Davy concludes from his experiments, (Elements, p. 280,) that the chloride of sulphur is composed of thirty parts of sulphur, and 68.4 of chlorine. This proportion leaves little doubt of its being a compound of 36, or one atom of chlorine, and of 16, or one atom of sulphur.

### *Compounds of Chlorine and Phosphorus.*

There are two definite compounds of chlorine and phosphorus, the nature of which was first satisfactorily explained by Sir H. Davy. (Elements, p. 290.) When phosphorus is introduced into a jar of dry chlorine, it inflames, and a white matter collects on the inside of the vessel, which is the *perchloride of phosphorus*. It is very volatile, a temperature much below 212° F. being sufficient to convert it into vapour. Under pressure it may be fused, and yields transparent prismatic crystals in cooling.

Water, and the perchloride of phosphorus mutually decompose each other; and the sole products are muriatic and phosphoric acids. The nature of the change will be apparent as soon as the composition of the perchloride is known. Sir H. Davy finds that one grain of phosphorus unites with six of chlorine when it is burned in that gas; and hence it follows that the perchloride consists of

Chlorine	.	72, or two atoms.
Phosphorus	.	12, or one atom.

Consequently, for every atom of the perchloride of phosphorus, two

\* Annals of Philosophy, second vol. N. S. p. 150.

† Nicholson's Journal, vol. vi.

‡ Mémoires d'Arcueil, vol. i.

atoms of water suffer decomposition. The two atoms of hydrogen unite with the two atoms of chlorine, and form two atoms of muriatic acid; while the two atoms of oxygen combine with the one atom of phosphorus, and convert it into phosphoric acid.

The *protochloride of phosphorus* may be made either by heating the perchloride with phosphorus, or by passing the vapour of phosphorus over corrosive sublimate contained in a glass tube. It is a clear liquid like water, which is composed, according to Sir H. Davy, of thirty-six parts or one atom of chlorine, and twelve parts or one atom of phosphorus. Its specific gravity is 1.45. It emits acid fumes when exposed to the air, owing to the decomposition of watery vapour; but when pure it does not redden dry litmus paper. On mixing it with water, mutual decomposition ensues, heat is evolved, and a solution of muriatic and phosphorous acids is obtained. In this case one atom of water is decomposed for each atom of the protochloride.

### *Chlorocarbonic Acid Gas.*

This compound was discovered in 1812 by Dr John Davy, who described it in the Philosophical Transactions for that year, under the name of *phosgene gas*\*. It is made by exposing a mixture of equal measures of dry chlorine and carbonic acid gases to sunshine, when a rapid but silent combination ensues, and they contract to one half their volume. The diffused day-light also effects their union slowly; but they do not combine at all when the mixture is wholly excluded from the light.

The *chlorocarbonic acid gas* is colourless, has a strong odour, and reddens dry litmus paper. It combines with four times its volume of ammoniacal gas, forming a white solid salt; so that it possesses the characteristic property of acids. It is decomposed by contact with water. One atom of each compound undergoes decomposition; and as the hydrogen of the water unites with chlorine, and its oxygen with carbonic oxide, the products are carbonic and muriatic acids. When tin is heated in chlorocarbonic acid gas, the chloride of tin is generated, and carbonic oxide gas is set free, which occupies exactly the same space as the chlorocarbonic acid which was employed. A similar change occurs when it is heated in contact with antimony, zinc or arsenic.

As chlorocarbonic acid gas contains its own volume of both its constituents, it follows that 100 cubic inches of that gas, at the standard temperature and pressure, must weigh 105.9 grains; namely, 76.25 of chlorine added to 29.65 of carbonic oxide. Its specific gravity is therefore 3.4721; and it is composed, atomically, of

Chlorine	36	or one atom.
Carbonic oxide	14	or one atom.

### *On the Nature of Chlorine.*

The change of opinion which has gradually taken place among chemists concerning the nature of chlorine, is a remarkable fact in the history of the science. The hypothesis of Berthollet, unfounded as it is, prevailed at one time universally. It explained phenomena so satisfactorily and in a manner so consistent with the received chemi-

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\* From  $\phi\omega\varsigma$  light and  $\gamma\epsilon\rho\rho\alpha\varsigma$  I produce.

cal doctrine, that for some years no one thought of calling its correctness into question. A singular reverse, however, has taken place. Though it has not hitherto been rigidly demonstrated to be erroneous, it has within a short period been generally abandoned, even by persons who, from having adopted it in early life, were prejudiced in its favour. The reason of this will readily appear on comparing the two theories, and examining the evidence in favour of each.

I. Chlorine, according to the new theory, is maintained to be a simple body, because, like oxygen, hydrogen, and other analogous substances, it cannot be resolved into more simple parts. It does not indeed follow that a body is simple, because it has not hitherto been decomposed; but as chemists have no other mode of estimating the elementary nature of bodies, they must necessarily adopt this one, or have none at all. Muriatic acid, according to the same doctrine, is considered to be a compound of chlorine and hydrogen. For when it is exposed to the agency of galvanism, it is resolved into these substances; and by mixing the two gases in due proportion, and passing an electric spark through the mixture, muriatic acid gas is the product. Chemists have no other kind of proof of the composition of water, of potassa, or of any other compound.

II. Very different is the evidence in support of the theory of Berthollet. According to that view, muriatic acid gas is composed of *absolute muriatic acid*, and water or its elements; chlorine consists of *absolute muriatic acid*, and oxygen; and *absolute muriatic acid* is a compound of a certain unknown base and oxygen gas. Now all these propositions are gratuitous. For, in the first place, muriatic acid gas has not been proved to contain water. Secondly, the assertion that chlorine contains oxygen is opposed to direct experiment, the most powerful deoxidizing agents having been unable to deprive that gas of a particle of oxygen. Thirdly, the existence of such a substance as *absolute muriatic acid* is wholly without proof, and therefore its supposed base is also imaginary.

But this is not the only weak point in the theory. Since chlorine is admitted by this theory to contain oxygen, it was necessary to explain how it happens that no oxygen can be separated from it. Thus, on exposing chlorine to a powerful galvanic battery, oxygen does not appear at the positive pole, as occurs when other oxidized bodies are subjected to its action; nor is carbonic acid or carbonic oxide evolved, when chlorine is conducted over ignited charcoal. To account for the oxygen not appearing under these circumstances, it was assumed that *absolute muriatic acid* is unable to exist in an uncombined state, and therefore cannot be separated from one substance except by uniting with another. This supposition was thought to be supported by the analogy of certain compounds, such as the nitric and oxalic acids, to the existence of which, unless combined with another body, water seems to be essential. It will be found, however, on close examination, that these instances are not applicable to the case of chlorine and muriatic acid. For though the nitric and oxalic acids have not hitherto been obtained free from water, this obviously arises from the tendency of their elements to obey other affinities, and to arrange themselves in a new order.

Admitting the various assumptions which have been stated, most of the phenomena receive as consistent an explanation by the old as by the new theory. Thus, when muriatic acid gas is resolved by galvanism into chlorine and hydrogen, it may be supposed that the *absolute*



*muratic acid* attaches itself to the oxygen of the water, and forms chlorine, while the hydrogen of the water is attracted to the opposite pole of the battery. When chlorine and hydrogen enter into combination, the oxygen of the former may be said to unite with the latter, and that *muratic acid* gas is generated by the water so formed combining with the *absolute muratic acid* of the chlorine. The evolution of chlorine, which ensues on mixing *muratic acid* and the peroxide of manganese, is explained on the supposition that *absolute muratic acid* unites directly with the oxygen of the black oxide of manganese.

It will not be difficult after these observations to account for the preference shown to the new theory. In an exact science, such as chemistry, every step of which is required to be matter of demonstration, there is no room to hesitate between two modes of reasoning, one of which is hypothetical, and the other founded on experiment. Nor is there, in the present instance, temptation to deviate from the strict logic of the science, for there is not a single phenomenon which may not be fully explained on the new theory, in a manner quite consistent with the laws of chemical action in general. It was supposed, indeed, at one time, that the sudden decomposition of water, occasioned by the action of that liquid on the compounds of chlorine with many simple substances, constitutes a real objection to the doctrine; but it will afterwards appear, that the acquisition of new facts has deprived this argument of all its force. While nothing therefore can be gained, much may be lost by adopting the doctrine of Berthollet. If chlorine is regarded as a compound body, the same opinion, though in direct opposition to the result of observation, ought to be extended to iodine; and as other analogous substances may hereafter be discovered, in regard to which a similar hypothesis will apply, it is obvious that this view, if proper in one case, may legitimately be extended to others. One encroachment on the method of strict induction would consequently open the way to another, and thus the genius of the science would eventually be destroyed.

An able attempt was made some years ago by the late Dr Murray, to demonstrate the presence of water or of its elements as a constituent part of *muratic acid* gas, and thus to establish the old theory to the subversion of the new. Into this discussion, however, I shall not enter here, as it would lead into details too minute for an elementary treatise. I shall only observe, in referring the reader to the original papers on the subject\*, that Dr Murray did not succeed in establishing his point; and that his arguments, though exceedingly plausible and ingenious, were fully answered by Sir Humphrey and Dr John Davy. I must also state, that the history of the only experiment which strictly bears upon the question,—that, namely, in which *muratic acid* and ammoniacal gases were mixed together,—amounts very nearly to a demonstration of the absence of combined water in *muratic acid* gas. The quantity of water which did make its appearance during the experiment, was so very small in comparison to what ought to have appeared on Dr Murray's supposition, as to leave little doubt in my mind that its origin was accidental.

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\* In Nicholson's Journal, vols. xxxi. xxxii. and xxxiv. Edinburgh Philos. Trans. vol. viii. and Philos. Trans. for 1818.

## SECTION XII.

## IODINE.

Iodine was discovered in 1812 by M. Courtois, a manufacturer of saltpetre at Paris. In preparing carbonate of soda from the ashes of sea weeds, he observed that the residual liquor corroded metallic vessels powerfully; and in investigating the cause of the corrosion, he noticed that sulphuric acid threw down a dark-coloured matter, which was converted by the application of heat into a beautiful violet vapour. Struck with its appearance, he gave some of the substance to M. Clément, who recognised it as a new body, and in 1813 described some of its leading properties in the Royal Institute of France. Its real nature was soon after determined by Gay-Lussac and Sir H. Davy, each of whom proved that it is a simple non-metallic substance, exceedingly analogous to chlorine\*.

Iodine, at common temperatures, is a soft friable opaque solid, of a bluish-black colour, and metallic lustre. It occurs usually in crystalline scales, having the appearance of micaceous iron-ore; but it sometimes crystallizes in large rhomboidal plates, the primitive form of which is an octahedron. Its specific gravity, according to Gay-Lussac, is 4.948; but Dr Thomson found it only 3.0814. At 225° F. it fuses, and enters into ebullition at 347° F.; but when moisture is present, it sublimes rapidly even below the degree of boiling water, and suffers a gradual dissipation at low temperatures. Its vapour is of an exceedingly rich violet colour, a character to which it owes the name of *Iodine*†. This vapour is remarkably dense, its specific gravity, as calculated by the formula of page 104, being 8.6102. Hence 100 cubic inches, at the standard temperature and pressure, must weigh 262.612 grains. Dr Thomson infers, partly from the experiments of Gay-Lussac, and partly from his own researches, that the atomic weight of iodine is 124.

Iodine is a non-conductor of electricity, and, like oxygen and chlorine, is a negative electric. It has a very acrid taste, and its odour is almost exactly similar to that of chlorine, when much diluted with air. It acts energetically on the animal system as an irritant poison, but is employed with advantage in medicine in very small doses.

Iodine is very sparingly soluble in water, requiring about 7000 times its weight of that liquid for solution. It communicates, however, even in this minute quantity, a brown tint to the menstruum. Alcohol and ether dissolve it freely, and the solution has a deep reddish-brown colour.

Iodine possesses an extensive range of affinity. It destroys vegetable colours, though in a much less degree than chlorine. It manifests little disposition to combine with metallic oxides; but it has a strong attraction for the pure metals, and for most of the simple non-metallic substances. These combinations are termed *Iodides* or *Iodurets*. It

\* The original papers on this subject are in the *Annales de Chimie*, vols. lxxxviii. xc. and xci.; and in the *Phil. Trans.* for 1814 and 1815.

† From *ἰώδης violaceus*.

is not inflammable; but under favourable circumstances may, like chlorine, be made to unite with oxygen. A solution of the pure alkalies acts upon it in the same manner as upon chlorine, giving rise to the decomposition of water and the formation of the iodic and hydriodic acids.

Pure iodine is not influenced chemically by the imponderables. Exposure to the direct solar rays, or to strong shocks of electricity, does not change its nature. It may be passed through red-hot tubes, or over intensely ignited charcoal, without any appearance of decomposition; nor is it affected by the agency of galvanism. Chemists, indeed, are unable to resolve it into more simple parts, and consequently it is regarded as an elementary principle.

The violet hue of the vapour of iodine is for many purposes a sufficiently sure indication of its presence. A far more delicate test, however, was discovered by MM. Colin and Gaultier de Claubry. They found that iodine has the property of uniting with starch, and of forming with it a compound insoluble in water, which is recognised with certainty by its deep blue colour. This test, according to Professor Stromeyer, is so delicate, that a liquid containing 1—450,000 of its weight of iodine, receives a blue tinge from a solution of starch. Two precautions should be observed to insure success. In the first place, the iodine must be in a free state; for it is the iodine itself only, and not its compounds, which unite with starch. Secondly, the solution should be quite cold at the time of adding the starch; for boiling water decomposes the blue compound, and consequently removes its colour.

### *Iodine and Hydrogen—Hydriodic Acid Gas.*

When a mixture of hydrogen and the vapour of iodine is transmitted through a red-hot porcelain tube, direct combination takes place between them, and a colourless gas, possessed of acid properties, is the product. To this substance the term *Hydriodic acid gas* is applied.

This gas may be obtained quite pure by the action of water on the iodine of phosphorus. Any convenient quantity of moistened iodine is put into a small glass retort, and about one-twelfth of its weight of phosphorus is then added. An iodine of phosphorus is formed, which instantly re-acts upon the water. Mutual decomposition ensues; the oxygen of the water unites with the phosphorus, and the hydrogen with the iodine, giving rise to the formation of phosphoric and hydriodic acids. On the application of a moderate heat, the latter passes over in the form of a colourless gas.

The hydriodic acid gas has a very sour taste, reddens vegetable blue colours without destroying them, and has an odour similar to that of muriatic acid gas. It combines with alkalies, forming salts which are called *hydriodates*. Like muriatic acid gas it cannot be collected over water; for that liquid dissolves it in large quantity.

Hydriodic acid is decomposed by several substances which have a strong affinity for either of its elements. Thus oxygen gas, when heated with it, unites with the hydrogen, and liberates the iodine. Chlorine effects the decomposition instantly; muriatic acid gas is produced, and the iodine appears in the form of vapour. It is also decomposed by mercury. The decomposition begins as soon as the hydriodic acid comes in contact with the mercury, and proceeds steadily, and even quickly if the gas is agitated, till nothing but hydrogen remains.

Gay-Lussac ascertained by this method that 100 measures of hydriodic acid gas contain precisely half their volume of hydrogen. This result induced him to suspect that the composition of hydriodic must be analogous to that of muriatic acid gas; that, as 100 measures of the latter contain 50 of hydrogen and 50 of chlorine, 100 measures of the former consist of 50 of hydrogen and 50 of the vapour of iodine. If this view be correct, then the composition of hydriodic acid gas, by weight, may be determined by calculation. For since

		<i>Grains.</i>
50	cubic inches of the vapour of iodine weigh	131.306
50	hydrogen gas	1.059
<hr/>		<hr/>
100	of hydriodic acid gas must weigh	132.365

and its specific gravity will be 4.3398. Now Gay-Lussac ascertained by weighing the hydriodic acid gas, that its density is 4.443,—a number which corresponds so closely to the preceding, as to leave no doubt that the principle of the calculation is correct. There is good reason to believe, indeed, that the calculated result, if not rigidly exact, is very near the truth; for Gay-Lussac states, that the number determined by him directly is too high. (*An. de Chimie*, vol. xci. p. 16.)

Since iodine and hydrogen unite in one proportion only, hydriodic acid is regarded as a compound of one atom of each element,—an opinion supported both by the proportions in which iodine combines with other substances, and by the analogy of muriatic acid. The constitution of hydriodic acid may therefore be thus stated:

	<i>By Volume.</i>	<i>By Weight.</i>
Iodine . . .	50 . . .	124 or one atom.
Hydrogen . . .	50 . . .	1 or one atom.
	<hr/>	<hr/>
	100	125

and its combining proportion is 125.

When hydriodic acid gas is conducted into water till that liquid is fully charged with it, a colourless acid solution is obtained, which emits white fumes on exposure to the air, and has a density of 1.7. It may be prepared also by passing a current of sulphuretted hydrogen gas through water in which iodine in fine powder is suspended. The iodine, from having greater affinity than sulphur for hydrogen, decomposes the sulphuretted hydrogen; and hence sulphur is set free, and hydriodic acid is produced. As soon as the iodine has disappeared, the solution is heated for a short time, to expel the excess of sulphuretted hydrogen, and subsequently filtered to separate the free sulphur.

The solution of hydriodic acid is readily decomposed. Thus, on exposure during a few hours to the atmosphere, the oxygen of the air forms water with the hydrogen of the acid, and sets iodine free. The solution is found to have acquired a yellow tinge from the presence of uncombined iodine, and a blue colour is occasioned by the addition of starch. The nitric and sulphuric acids likewise decompose it by yielding oxygen, the former being at the same time converted into nitrous, and the latter into sulphurous acid. Chlorine unites directly with the hydrogen of the hydriodic acid, and muriatic acid is formed. The separation of iodine in all these cases may be proved in the way just mentioned. These circumstances afford a sure test of the presence of hydriodic acid, whether free or in combination with alkalies. All that

is necessary, is to mix a cold solution of starch with the liquid, previously concentrated by evaporation if necessary, and then to add a few drops of strong sulphuric acid. A blue colour will make its appearance if hydriodic acid is present.

Hydriodic acid is frequently met with in nature in combination with potassa or soda. Under this form it occurs in many salt and other mineral springs. It has been detected in the water of the Mediterranean, in the oyster and some other marine molluscous animals, in sponges, and in most kinds of sea-weed. In some of these productions, such as the *Fucus serratus* and *Fucus digitatus*, it exists ready formed, and according to Dr Fyfe (Edinburgh Philos. Journal, vol. i.) may be separated by the action of water; but in others it can be detected only after incineration. The marine animals and plants doubtless derive the hydriodic acid they contain from the sea. Vauquelin has found it also in the mineral kingdom, in combination with silver. (Annales de Chimie et de Physique, vol. xxiv.)

All the iodine of commerce is procured from the impure carbonate of soda, called kelp, which is prepared in large quantity on the northern shores of Scotland, by incinerating sea-weeds. The kelp is employed by soap-makers for the preparation of carbonate of soda; and the dark residual liquor, remaining after that salt has crystallized, contains a considerable quantity of hydriodic acid, combined with soda or potash. By adding a sufficient quantity of sulphuric acid, the hydriodic acid is separated from the alkali, and then decomposed. The iodine sublimes when the solution is boiled, and may be collected in cool glass receivers. A more convenient process is to employ a moderate excess of sulphuric acid, and then add some of the peroxide of manganese to the mixture. The oxygen of the manganese decomposes the hydriodic acid, and a protosulphate of manganese is formed. (Dr Ure's Paper in the 50th volume of the Philosophical Magazine.)

### *Iodine and Oxygen.—Iodic Acid.*

Iodic acid was discovered about the same time by Gay-Lussac, and Sir H. Davy; but the latter first succeeded in obtaining it in a perfectly pure state. When iodine is brought into contact with the protoxide of chlorine, an immediate action ensues; the chlorine of the protoxide unites with one portion of iodine, and its oxygen with another, forming two compounds, a volatile orange-coloured matter, the chloride of iodine, and a white solid substance, which is *iodic acid*. On applying heat, the former passes off in vapour, and the latter remains. (Philos. Trans. for 1815.)

This compound, which was termed *oxiodine* by Sir H. Davy, is *anhydrous iodic acid*. It is a white semitransparent solid, which has a strong astringent sour taste, but no odour. Its density is considerable, as it sinks rapidly in sulphuric acid. When heated to the temperature of about 500° F., it fuses, and at the same time is resolved into oxygen and iodine.

Iodic acid deliquesces in a moist atmosphere, and is very soluble in water. The liquid acid thus formed reddens vegetable blue colours, and afterwards destroys them. On evaporating the solution, a thick mass of the consistence of paste is left, which is hydrous iodic acid, and from which, by cautious application of heat, the water may be expelled. It acts powerfully on inflammable substances. With charcoal, sulphur, sugar, and similar combustibles, it forms mixtures which



detonate when heated. It enters into combination with metallic oxides, and the resulting salts are called *iodates*. These compounds like the chlorates yield pure oxygen by heat, and deflagrate when thrown on burning charcoal.

Iodic acid unites with several of the acids, such as the sulphuric, nitric, phosphoric, and boracic acids; and with the three first it forms crystallizable compounds. It is decomposed by the sulphurous, phosphorous, and hydriodic acids, and by sulphuretted hydrogen. Iodine in each case is set at liberty, and may be detected as usual by starch. The muriatic and iodic acids decompose each other, water and chloriodic acid being generated.

Sir H. Davy analyzed iodic acid by determining the quantity of oxygen which it evolves when decomposed by heat. Gay-Lussac effected the same object by heating the iodate of potash, when pure oxygen was given off, and the iodide of potassium remained. From the result of these analyses, it appears that iodic acid is a compound of one atom of iodine and five atoms of oxygen; so that its elements are in the proportion of

Iodine	.	124, or one atom.
Oxygen	.	40, or five atoms.

and its atomic weight is 164.

*Iodous acid.* The iodous acid is prepared by triturating iodine with an equal weight of the chlorate of potassa in a glass or porcelain mortar, until they form a very fine pulverulent yellow mass, in which the metallic lustre of the iodine is no longer perceptible. The mixture is then heated in a glass retort; and as soon as the chlorate begins to lose oxygen, the iodous acid rises in the form of a dense white vapour, and condenses in the neck of the retort into a yellow liquid, which falls in drops into the receiver.

The iodous acid is a yellow liquid of an oily consistency, and of a peculiarly disagreeable odour, somewhat resembling euchlorine. It has an acid astringent taste, and leaves a burning sensation on the tongue. It reddens vegetable blue colours permanently, without destroying them. With water and alcohol it forms amber-coloured solutions. Its density is greater than that of water. It volatilizes rapidly at 212° F. and evaporates slowly at common temperatures. Sulphur decomposes it, and phosphorus and potassium take fire as soon as they come in contact with it.

The iodous acid, the composition of which has not yet been determined, was discovered in 1824 by Professor Sementini of Naples, (*Quarterly Journal*, vol. xvii. p. 381.) The same chemist is of opinion that an oxide of iodine is formed by the action of sulphurous acid on iodous acid; but this requires further investigation.

### *Chloriodic Acid.*

Chlorine is absorbed at common temperatures by dry iodine with evolution of caloric, and a solid compound of iodine and chlorine results, which was discovered both by Sir H. Davy and Gay-Lussac. The colour of the product is orange-yellow when the iodine is fully saturated with chlorine, but is of a reddish-orange if the iodine is in excess. It is converted by heat into an orange-coloured liquid which yields a vapour of the same tint on an increase of temperature. It deliquesces in the open air, and dissolves freely in water. Its solution

is colourless, is very sour to the taste, and reddens vegetable blue colours, but afterwards destroys them. From its acid properties Sir H. Davy gave it the name of *chloriodic acid*. Gay-Lussac on the contrary calls it *chloride of iodine*, conceiving that the acidity of its solution arises from the presence of muriatic and iodic acids, which he supposes to be generated by the decomposition of water. The opinion of Sir H. Davy appears to me more probable; for we know that free muriatic and iodic acids mutually decompose each other, and therefore could hardly be generated by the action of water on the compound of iodine and chlorine. The chloriodic acid, however, does not unite with alkaline substances. On mixing it, for example, with baryta, the muriate and iodate of baryta are obtained. From this it may be inferred, that water and chloriodic acid react on each other when an alkali is added to them.

The composition of chloriodic acid is not known with precision.

*Iodide of nitrogen.* From the weak affinity that exists between iodine and nitrogen, these substances cannot be made to unite directly. But when iodine is put into a solution of ammonia, the alkali is decomposed; its elements unite with different portions of iodine, and thus cause the formation of hydriodic acid and iodide of nitrogen. The latter subsides in the form of a dark powder, which is characterised, like the chloride of nitrogen, by its explosive property. It detonates violently as soon as it is dried, and slight pressure, while moist, produces a similar effect. Heat and light are emitted during the explosion, and iodine and nitrogen are set free. According to the experiments of M. Colin, the iodide of nitrogen consists of one atom of nitrogen to three of iodine.

*Iodide of phosphorus.* Iodine and phosphorus combine readily in the cold, evolving so much caloric as to kindle the phosphorus if the experiment is made in the open air; but in close vessels no light appears. The combination takes place in several proportions, which have not been determined. Its most interesting property is that of decomposing water, with formation of hydriodic and phosphoric acids.

*Iodide of sulphur.* This compound is formed by heating gently a mixture of iodine and sulphur. The product has a dark colour and radiated appearance, like antimony. Its elements are easily disunited by heat.

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## SECTION XIII.

### *FLUORINE, OR THE BASE OF FLUORIC ACID.*

The base of fluoric acid has never been obtained in a separate state, and so little is known concerning it, that its real nature is at present involved in much obscurity. The history of this body must therefore be confined to a description of its compounds. Of these, the principal is *fluoric acid*.

Fluoric acid was discovered in the year 1771 by Scheele, but Gay-Lussac and Thénard first obtained it in a pure form\*. It is prepared

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\* *Recherches Physico-Chimiques*, vol. ii.

by acting upon the mineral called *fluor spar*, carefully separated from silicious earth and reduced to a fine powder, with twice its weight of concentrated sulphuric acid. The mixture is made in a leaden retort; and on applying heat, an acid vapour distils over, which must be collected in a receiver of the same metal, surrounded by ice. At the close of the operation, a dry mass, the sulphate of lime, is found in the retort; while the receiver contains fluoric acid, dissolved, according to Gay-Lussac and Thénard, in the water of the sulphuric acid. The fluor-spar is regarded by these chemists as a compound of fluoric acid and lime, and consequently the sulphuric acid is supposed merely to decompose the salt by uniting with its base.

Fluoric acid, at the temperature of 32° F. is a colourless fluid, and remains in that state at 59° F. if preserved in well-stopped bottles; but when it is exposed to the air, it flies off in dense white fumes, which consist of the vapour of the acid in combination with the moisture of the atmosphere. Its specific gravity is 1.0609; but its density may be increased to 1.25 by gradual additions of water. Its affinity for water is far greater than that of the strongest sulphuric acid. When one drop of it falls into water, a hissing noise is heard similar to what is occasioned by plunging a red hot iron into that liquid.

The vapour of fluoric acid is pungent in the extreme, far more so than chlorine or any of the gases. Of all known substances, fluoric acid is the most destructive to animal matter. When a drop of the concentrated acid, of the size of a pin's head, comes in contact with the skin, instantaneous disorganization ensues, followed by deep ulceration, which is very difficult to heal.

Concentrated fluoric acid acts energetically on glass. The transparency of the glass is instantly destroyed, caloric is evolved, and the acid boils, and in a short time disappears entirely, a colourless gas being the sole product. This gas has received the name of *fluosilicic acid gas*, because it is regarded as a compound of fluoric acid and silica. It is always formed when fluor-spar and sulphuric acid are heated together in a glass vessel, or when fluor-spar itself is mixed with silicious earth. This is the substance which Scheele always procured in his process, and which he supposed to be fluoric acid. From the strong affinity of fluoric acid for silica, it cannot be preserved in glass bottles; and should therefore be kept in vessels of lead or silver. For the same reason fluoric acid may be employed for etching on glass.

Fluoric acid is in every respect a powerful acid. It has a strong sour taste, reddens litmus paper, and forms salts with alkalies, which are termed *fluates*. All these salts are decomposed by strong sulphuric acid with the aid of heat, and the fluoric acid while escaping may be detected by its action on glass. According to the experiments of Dr Thomson, 10 is the combining proportion of fluoric acid.

As all other acids are compound, Gay-Lussac and Thénard naturally regarded the fluoric acid as such also, and adopted the opinion that it is composed of a certain combustible body and oxygen gas. They accordingly attempted to decompose it by means of some substance which has a strong affinity for oxygen, and employed potassium for that purpose. When that metal is brought into contact with fluoric acid, a violent action ensues, accompanied with an explosion, unless the experiment is cautiously conducted;—hydrogen gas is disengaged, and a white solid is produced, which has all the properties of fluato of potassa. The explanation which Gay-Lussac and Thénard gave of these phenomena is, that the hydrogen arises from the decom-

position of water, that the oxygen of that fluid combines with the potassium, and that the potassa so formed unites with the fluoric acid. They infer, therefore, from their experiments, that the strongest fluoric acid hitherto prepared contains water.

A different view of the nature of fluoric acid, originally suggested by M. Ampère of Paris, has been proposed by Sir H. Davy\*. This philosopher contends that fluoric acid, in its strongest form, is anhydrous; for on combining it with ammoniacal gas, a dry fluato of ammonia is formed, from which no water can be expelled by heat. He maintains also, that fluoric acid is composed, not of an inflammable base and oxygen, but of hydrogen united with a negative electric body, analogous to chlorine, to which he has given the name of *fluorine*. According to this theory, fluor-spar is a *fluoride* of calcium, that is, a compound of fluorine and the metallic base of lime. When sulphuric acid decomposes it, the water which it contains is resolved into its elements. The hydrogen unites with fluorine, by which the fluoric (or the *hydrofluoric*) acid is generated; while the oxygen unites with the calcium, and forms lime. When the metal potassium is brought into contact with fluoric acid, the hydrogen is not derived from water but from the acid; and the supposed fluato of potassa is a compound of fluorine and potassium.

Sir H. Davy has supported his opinion by many ingenious arguments; but the only direct experiment in proof of the existence of fluorine is the following: On exposing fluoric acid to the agency of galvanism, there was a disengagement at the negative pole of a small quantity of gas, which was inferred from its combustibility to be hydrogen; while the platinum wire of the opposite side of the battery was rapidly corroded, and became covered with a chocolate-coloured powder. Sir H. Davy explains these phenomena by supposing the fluoric acid to have been resolved into its elements, and that the fluorine, at the moment of arriving at the positive end of the battery, entered into combination with the platinum wire which was employed as a conductor. Unfortunately, however, he did not succeed in obtaining fluorine in an insulated state, and therefore its existence is questionable. Indeed, from the noxious vapours that arose during the experiment, it was impossible to watch its progress and examine the different results with that precision which is essential to the success of minute chemical inquiries, and which Sir H. Davy has so frequently displayed on other occasions. These circumstances appear to justify the opinion adopted, I believe, by most chemists, that experiments of a more decisive kind are required for determining the nature of fluoric acid with certainty.

In this state of the inquiry, it is not important by which doctrine the phenomena are explained. On the whole, the arguments preponderate in favour of the view proposed by Sir H. Davy; but as the other theory was first introduced, and is in general more easily understood by chemical students, I shall retain it here.

### *Fluo-Boric Acid Gas.*

One difficulty in determining the nature of fluoric acid arises from the water of the sulphuric acid which is employed in its preparation. To

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\* Philosophical Transactions for 1813, 1814.

avoid this source of uncertainty, Gay-Lussac and Thénard made a mixture of vitrified boracic acid and fluuate of lime, and exposed it in a leaden retort to heat, under the expectation that as no water was present, anhydrous fluoric acid would be obtained. In this however they were disappointed; but a new gas came over, to which Gay-Lussac and Thénard applied the term of *fluo-boric acid gas*. A similar train of reasoning led Sir H. Davy about the same time to the same discovery; though Gay-Lussac and Thénard had the advantage in priority of publication. Fluo-boric acid gas may be prepared more conveniently by mixing one part of vitrified boracic acid, and two of fluor-spar with twelve parts of strong sulphuric acid, and heating the mixture gently in a glass retort. (Dr John Davy, Phil. Trans. for 1812.)

Fluo-boric acid gas is colourless, has a penetrating pungent odour, and extinguishes flame on the instant. It reddens litmus paper as powerfully as sulphuric acid, and forms salts with alkalies which are called *fluo-borates*. It has a singularly great affinity for water. When it is mixed with air or any gas which contains watery vapour, a dense white cloud appears, which is a combination of water and fluo-boric acid gas. From this circumstance it forms an exceedingly delicate test of the presence of moisture in gases. Fluo-boric acid gas is rapidly absorbed by water. According to Dr John Davy, water absorbs 700 times its volume. Caloric is evolved during the absorption, and the water acquires an increase of volume. The saturated solution is limpid, fuming, and very caustic.

Fluo-boric acid gas does not act on glass, but attacks animal and vegetable matters with energy, converting them like sulphuric acid into a carbonaceous substance. This action is most probably owing to its affinity for water.

When potassium is heated in fluo-boric acid gas it inflames, and a chocolate-coloured solid, wholly devoid of metallic lustre, is the sole product. On putting this substance into water, a part of it dissolves, and a solution is obtained, which has all the characters of the fluuate of potassa. The insoluble matter is boron. From this and other experiments, fluo-boric acid gas is inferred to be a compound of fluoric and boracic acids. It is presumed likewise, that when potassium burns in this gas, the oxygen is derived from the boracic acid, and that the potassa so formed unites directly with the fluoric acid. It is also evident, according to this view, that in the processes for forming fluo-boric acid gas, the fluoric acid, at the moment of separation from the lime, unites directly with boracic acid. The explanation given by Sir H. Davy is different. He regards fluo-boric acid gas as a compound of fluorine and boron, and ascribes the combustion of potassium in it to the combination of that metal with fluorine.

The specific gravity of fluo-boric acid gas was found by Dr John Davy to be 2.3709, and by Dr Thomson, 3.3622. By calculation Dr Thomson states its real density at 2.3611, an estimate which is probably correct. Consequently, 100 cubic inches of fluo-boric acid gas, at 60° F., and when the barometer stands at 30 inches, must weigh 72.0135 grains. From the experiments of the same chemist (First Principles, vol. ii.) this compound consists of

Boracic acid	.	.	24 or one atom.
Fluoric acid	.	.	10 or one atom.

and hence its combining proportion is 34.



## ON THE COMPOUNDS OF THE SIMPLE NON-METALLIC ACIDIFIABLE COMBUSTIBLES WITH EACH OTHER.

### SECTION I.

#### HYDROGEN AND NITROGEN—AMMONIACAL GAS.

THE *spirit of hartshorn* has been long familiar to chemists ; but the existence of ammonia as a gas was first noticed by Dr Priestley, and was described by him in his works under the name of *alkaline air*. It is sometimes called the *volatile alkali* ; but the terms *ammonia* and *ammoniacal gas* are now more commonly employed.

The most convenient method of preparing ammoniacal gas for the purposes of experiment is by applying a gentle heat to the concentrated solution of ammonia, contained in a glass vessel. It soon enters into ebullition, and a large quantity of pure ammonia is disengaged.

Ammonia is a colourless gas, which has a strong pungent odour, and acts powerfully on the eyes and nose. It is quite irrespirable in its pure form, but when diluted with air, it may be taken into the lungs with safety. Burning bodies are extinguished by it, nor is the gas inflamed by their approach. Ammonia, however, is inflammable in a low degree. For when a lighted candle is immersed in it, the flame is somewhat enlarged, and tinged of a pale yellow colour at the moment of being extinguished ; and a small jet of the gas will burn in an atmosphere of oxygen. A mixture of ammoniacal and oxygen gases detonates by the electric spark ; water is formed, and nitrogen remains. A little nitric acid is generated at the same time, except when less oxygen is employed than is sufficient for combining with all the hydrogen of the ammonia. (Dr Henry in the *Philos. Trans.* for 1809.)

Ammoniacal gas at the temperature of 50° F. and under a pressure equal to 6.5 atmospheres, becomes a transparent colourless liquid. It is also liquefied, according to Guyton-Morveau, under the common pressure, by a cold of 70 degrees below zero of Fahrenheit ; but it is more probable that the liquid he obtained was a solution of ammonia in water.

Ammonia has all the properties of an alkali in a very marked manner. Thus it has an acid taste, and gives a brown stain to turmeric paper ; though the yellow colour soon reappears on exposure to the air, owing to the volatility of the alkali. It combines also with acids, and neutralizes their properties completely. All these salts suffer decomposition by being heated with the fixed alkalies or alkaline earths, such as potassa or lime. These substances unite with the acid of the salt, and the ammonia is expelled. None of the ammoniacal salts can sustain a red heat without being dissipated in vapour or decomposed, a character which manifestly arises from the volatile nature of the

alkali. If it is combined with a volatile acid, such as the muriatic, then the compound itself sublims unchanged by heat; but if it is in combination with an acid, such as the phosphoric, which is fixed in the fire, in that case the ammonia alone is expelled.

Hydrogen and nitrogen gases do not unite directly, and therefore chemists have no synthetic proof of the constitution of ammonia. Its composition, however, has been determined analytically with great exactness. When a succession of electric sparks is passed through ammoniacal gas, it is resolved into its elements; and the same effect is produced by conducting ammonia through porcelain tubes heated to redness. The late A. Berthollet analyzed ammonia in both ways, and ascertained that 200 measures of that gas, on being decomposed, occupy the space of 400 measures, 300 of which are hydrogen, and 100 nitrogen. Dr Henry has very recently made an analysis of ammonia by means of electricity, and his experiment proves beyond a doubt that the proportions above given are rigidly exact. (*Annals of Philosophy*, N. S. vol. viii.)

					<i>Grains.</i>
Now since 150 cubic inches of hydrogen weigh	.				3.177
50 nitrogen	.	.	.	.	14.826
					<hr/>
100 cubic inches of ammonia must weigh					18.003

and it is composed by weight of

Hydrogen	.	3.177	.	3	.	3 atoms.
Nitrogen	.	14.826	.	14	.	one atom.

The weight of its atom, therefore, is 17.

The specific gravity of ammonia, according to this calculation, is 0.5902, a number which agrees closely with those ascertained directly by Sir H. Davy and Dr Thomson.

Ammoniacal gas has a powerful affinity for water, and for this reason must always be collected over mercury. Owing to this attraction, a piece of ice, when introduced into a jar full of ammonia, is instantly liquefied, and the gas disappears in the course of a few seconds. Sir H. Davy, in his elements, states that water at 50° F. and when the barometer stands at 29.8 inches, absorbs 670 times its volume of ammonia; and that the solution has a specific gravity of 0.875. According to Dr Thomson, water at the common temperature and pressure takes up 780 times its bulk. By strong compression water absorbs the gas in still greater quantity. Caloric is evolved during the absorption, and a considerable expansion, independently of the increased temperature, occurs at the same time.

The concentrated solution of ammonia, commonly, though incorrectly, termed *liquid ammonia*, is made by passing a current of the gas, as long as it continues to be absorbed, into distilled water, which is kept cool by means of ice or moist cloths. The gas may be prepared from any salt of ammonia by the action of any pure alkali or alkaline earth; but muriate of ammonia and lime, from economical considerations, are always employed. The proportions to which I give the preference are equal parts of the muriate of ammonia and well-burned quicklime, a considerable excess of lime being taken, in order to decompose the muriate more expeditiously and completely. The lime is slaked by the addition of water, and as soon as it has fallen into pow-

der, it should be placed in an earthen pan and be covered to protect it from the carbonic acid of the air, till it is quite cold. It is then mixed in a mortar with the muriate of ammonia, previously reduced to a fine powder, and the mixture is put into a retort or other convenient glass vessel. Heat is then applied, and the temperature gradually increased as long as a free evolution of gas continues. The ammonia should be conducted by means of a Welter's safety tube into a quantity of distilled water equal to the weight of the salt employed. The residue consists of lime and muriate of lime.

The concentrated solution of ammonia, as thus prepared, is a clear colourless liquid, of specific gravity 0.936. It possesses the peculiar pungent odour, taste, alkalinity, and other properties of the gas itself. On account of its great volatility it should be preserved in well-stopped bottles, a measure which is also required to prevent the absorption of carbonic acid. At a temperature of 130° F. it enters into ebullition, owing to the rapid escape of pure ammonia; but the whole of the gas cannot be expelled by this means, as at last the solution itself evaporates. It freezes at about the same temperature as mercury.

The following table, from Sir H. Davy's Elements of Chemical Philosophy, shows the quantity of real ammonia contained in 100 parts of solutions of different densities, at 59° F. and when the barometer stands at 30 inches. The specific gravity of water is supposed to be 10,000 :—

*Table of the quantity of real Ammonia in solutions of different densities.*

100 parts of sp. gravity.		of real Ammonia.	100 parts of sp. gravity.		of real Ammonia.
8750	contain	32.5	9435	contain	14.53
8875	“ “	29.25	9476	“ “	13.46
9000	“ “	26.00	9513	“ “	12.40
9054	“ “	25.37	9545	“ “	11.56
9166	“ “	22.07	9573	“ “	10.82
9255	“ “	19.54	9597	“ “	10.17
9326	“ “	17.52	9619	“ “	9.60
9385	“ “	15.88	9692	“ “	9.50

The presence of free ammoniacal gas may always be detected by its odour, by its temporary action on the yellow turmeric paper, and by forming dense white fumes, the muriate of ammonia, when a glass rod moistened with muriatic acid is brought near it.

## SECTION II.

### COMPOUNDS OF HYDROGEN AND CARBON.

Chemists have for several years been acquainted with two distinct compounds of carbon and hydrogen, the carburetted hydrogen and olefiant gas; but the researches of Mr Faraday have quite recently enriched the science by the discovery of two new substances of a similar

nature, and the same able chemist has demonstrated the existence of others, though he has hitherto been unable to obtain them in an insulated form. According to Dr Thomson, naphtha and naphthaline are likewise pure carburets of hydrogen.

### Light Carburetted Hydrogen.

This gas is sometimes called *heavy inflammable air*, the *inflammable air of marshes*, *hydro-carburet*, and *proto-carburet of hydrogen*. Dr Thomson proposed the term of *bi-hydroguret of carbon*; but it is more generally known by the name of *light carburetted hydrogen*. It is formed abundantly in stagnant pools during the spontaneous decomposition of dead vegetable matter; and it may readily be procured by stirring the mud at the bottom of them, and collecting the gas, as it escapes, in an inverted glass vessel. In this state it is found to contain 1-20th of carbonic acid gas, which may be removed by means of lime water or a solution of pure potassa, and 1-15th or 1-20th of nitrogen. This is the only convenient method of obtaining it.

Light carburetted hydrogen is tasteless and nearly inodorous, and it does not change the colour of litmus or turmeric paper. Water, according to Dr Henry, absorbs about 1-60th of its volume. It extinguishes all burning bodies, and is of course unable to support the respiration of animals. It is highly inflammable, and when a jet of it is set on fire, it burns with a yellow flame, and with a much stronger light than is occasioned by hydrogen gas. With a due proportion of atmospheric air or oxygen gas it forms a mixture which detonates powerfully with the electric spark, or by the contact of flame. The sole products of the explosion are water and carbonic acid.

Mr Dalton first ascertained the real nature of light carburetted hydrogen, and it has since been particularly examined by Dr Thomson, Sir H. Davy, and Dr Henry. When 100 measures are detonated with rather more than twice their volume of oxygen, the whole of the inflammable gas, and precisely 200 measures of the oxygen disappear, water is condensed, and 100 measures of carbonic acid are produced. From this it may be inferred (pages 102 and 103), that 100 cubic inches of light carburetted hydrogen contain 100 cubic inches of the vapour of carbon and 200 cubic inches of hydrogen; and that it is composed by weight of

Carbon	.	.	6	or one atom.
Hydrogen	.	.	2	or two atoms.

Its atomic weight is consequently 8.

From the same data it follows that 100 inches of light carburetted hydrogen, at 60 F., and when the barometer stands at 30 inches, must weigh 16.939 grains, and its specific gravity is therefore 0.5554. This calculated result is almost identical with the density of the gas as determined directly by Dr Henry and Dr Thomson.

Light carburetted hydrogen is not decomposed by electricity, or by being passed through red hot tubes, unless the temperature is very great. It may be inferred from the experiments of Berthollet, and from the phenomena that attend the formation of oil gas at high temperatures, that light carburetted hydrogen is resolved into its elements, at least in part, when the heat is very intense. It follows from the

nature of the gas, that for each volume so decomposed, two volumes of hydrogen must be set free.

Chlorine and light carburetted hydrogen do not act on each other at common temperatures, when quite dry, even if they are exposed to the direct solar rays. If the gases are moist, and the mixture is kept in a dark place, still no action ensues; but if light be admitted, particularly sunshine, then decomposition follows. The nature of the products depends upon the proportion of the gases. If four measures of chlorine and one of light carburetted hydrogen are present, carbonic and muriatic acid gases will be produced,—effects which may be thus explained. Two volumes of chlorine combine with two volumes of hydrogen contained in the carburetted hydrogen, and the other two volumes of chlorine decompose so much water as will likewise give two volumes of hydrogen,—which forms muriatic acid; while the oxygen of the water unites with the carbon, and converts it into carbonic acid. If there are three instead of four volumes of chlorine, then carbonic oxide will be generated instead of carbonic acid, because one-half less water will be decomposed. (Dr Henry.) If a mixture of chlorine and light carburetted hydrogen is electrified or exposed to a red heat, muriatic acid is formed, and charcoal is deposited.

It was first ascertained by Dr Henry (Nicholson's Journal, vol. xix.), and his conclusions have been fully confirmed by the subsequent researches of Sir H. Davy, that the *fire-damp* of coal mines consists almost solely of light carburetted hydrogen. This gas often issues in enormous quantity from between beds of coal, and by collecting in mines, owing to deficient ventilation, gradually mingles with atmospheric air, and forms an explosive mixture. The first unprotected light which then approaches, sets fire to the whole mass, and a dreadful explosion ensues. These accidents, which were formerly so frequent and so fatal, are now comparatively rare, owing to the employment of the safety lamp; and I conceive it to be demonstrable, on the view that light carburetted hydrogen is the sole constituent of fire-damp, that accidents of the kind cannot occur at all, provided the gauze lamp is in a due state of repair, and is employed with the requisite precautions. For this invention we are indebted to Sir H. Davy; and we must in justice remember that it is not, like many discoveries, the offspring of chance, but the fruit of elaborate experiment and close induction, which originated solely with that philosopher, and which may be regarded as one of the happiest efforts of his genius. (Essay on Flame.)

Sir H. Davy commenced the inquiry by determining the best proportion of air and light carburetted hydrogen for forming an explosive mixture. When the inflammable gas is mixed with three or four times its volume of air, it does not explode at all. It detonates feebly when mixed with five or six times its bulk of air, and powerfully when one to seven or one to eight is the proportion. With 14 times its volume, it still forms a mixture which is explosive; but if a larger quantity of air be admitted, a taper burns in it only with an enlarged flame.

The temperature which is required for causing an explosion was next ascertained. It was found that the strongest explosive mixture might come in contact with iron or other solid bodies heated to redness, or even to whiteness, without detonating, provided they are not in a state of actual combustion; whereas the smallest point of flame, owing to its higher temperature, instantly causes an explosion.

The last important step in the inquiry was the observation that flame



cannot pass through a narrow tube. This led Sir H. Davy to the discovery that the power of tubes in preventing the transmission of flame is not necessarily connected with any particular length; and that a very short one will have the effect, provided its diameter is proportionally reduced. Thus a piece of fine wire gauze, which may be regarded as an assemblage of short small tubes, is quite impermeable to flame; and consequently if a common oil lamp be completely surrounded with a cage of such gauze, it may be introduced into an explosive atmosphere of fire-damp and air, without kindling the mixture. This simple contrivance, which is appropriately termed the *safety-lamp*, not only prevents explosion, but indicates the precise moment of danger. When the lamp is carried into an atmosphere charged with fire-damp, the flame begins to enlarge; and the mixture, if highly explosive, takes fire as soon as it has passed through the gauze and burns on its inner surface, while the light in the centre of the lamp is extinguished. Whenever this appearance is observed, the miner must instantly withdraw; for though the flame cannot communicate to the explosive mixture on the outside of the lamp, as long as the texture of the gauze remains entire, yet the heat emitted during the combustion is so great, that the wire, if exposed to it for a few minutes, would suffer oxidation, and fall to pieces.

The peculiar operation of small tubes in obstructing the passage of flame admits of a very simple explanation. Flame is gaseous matter heated so intensely as to be luminous; and Sir H. Davy has shown that the temperature necessary for producing this effect is far higher than the white heat of solid bodies. Now when flame comes in contact with the sides of very minute apertures, as when wire gauze is laid upon a burning jet of coal gas, it is deprived of so much caloric that its temperature instantly falls below the degree at which gaseous matter is luminous; and consequently, though the gas itself passes freely through the interstices, and is still very hot, it is no longer incandescent. Nor does this take place when the wire is cold only;—the effect is equally certain at any degree of heat which the flame can communicate to it. For since the gauze has a large extent of surface, and from its metallic nature is a good conductor of caloric, it loses heat with great rapidity. Its temperature, therefore, though it may be heated to whiteness, is always so far below that of flame, as to exert a cooling influence over the burning gas, and thus deprive it of its property of emitting light.

### *Olefiant Gas.*

This gas was discovered in 1796 by some associated Dutch chemists, who gave it the name of *Olefiant gas*, from its property of forming an oily-like liquid with chlorine. It is sometimes called *bi-carburetted* or *per-carburetted hydrogen*, and *hydroguret of carbon*; but as none of these terms convey a precise idea of its nature, I shall employ the appellation proposed by its discoverers.

Olefiant gas is prepared by mixing in a capacious retort six measures of strong alcohol with sixteen of concentrated sulphuric acid, and heating the mixture as soon as it is made by means of an Argand lamp. The acid soon acts upon the alcohol, effervescence ensues, and olefiant gas passes over. The chemical changes which take place are of a complicated nature, and the products numerous. At the commencement of the process, the olefiant gas is mixed only with a little



Olefiant gas, by weight, consists of

Carbon	.	25.418	.	12 or two atoms.
Hydrogen	.	4.236	.	2 or two atoms.

and therefore 14 is the weight of its atom.

Olefiant gas, when a succession of electric sparks is passed through it, is resolved into charcoal and hydrogen; and the latter of course occupies twice as much space as the gas from which it was derived. Olefiant gas is decomposed by being passed through red-hot tubes of porcelain. The nature of the products depends upon the temperature. By employing a very low degree of heat, it may probably be converted solely into carbon and light carburetted hydrogen; and in this case no increase of volume can occur, because these two gases, for equal bulks, contain the same quantity of hydrogen. But if the temperature is high, then a great increase of volume takes place, a circumstance which indicates the evolution of free hydrogen, and consequently the total decomposition of some of the olefiant gas.

Chlorine acts powerfully on olefiant gas. When these gases are mixed together in the proportion of two measures of the former to one of the latter, they form a mixture which takes fire on the approach of flame, and which burns rapidly with formation of muriatic acid gas, and deposition of a large quantity of charcoal. But if the gases are allowed to remain at rest after being mixed together, a very different action ensues. The chlorine, instead of decomposing the olefiant gas, enters into direct combination with it, and a yellow liquid like oil is generated. This substance is sometimes called *chloric ether*; but the term *hydrocarburet of chlorine*, as indicative of its composition, is more appropriate.

The hydrocarburet of chlorine was discovered by the Dutch chemists; but Dr Thomson\* first ascertained that it is a compound of olefiant gas and chlorine; and its nature has since been more fully elucidated by the researches of MM. Robiquet and Colin†. To obtain it in a pure and dry state, it should be well washed with water, and then distilled from the chloride of calcium. As thus purified, it is a colourless volatile liquid, of a peculiar sweetish taste and ethereal odour. Its specific gravity at 45° F. is 1.2201. It boils at 152° F., and may be distilled without change. It suffers complete decomposition when its vapour is passed through a red-hot porcelain tube, being resolved into charcoal, light carburetted hydrogen, and muriatic acid gas.

The composition of the hydrocarburet of chlorine is readily inferred from the fact, that in whatever proportions olefiant gas and chlorine may be mixed together, they always unite in equal volumes. Consequently they combine by weight according to the ratio of their densities, so that the hydrocarburet of chlorine consists of

Chlorine	.	.	.25	.	36 one atom.
Olefiant gas	.	.	0.9722	.	14 one atom.
			<hr/>		<hr/>
			3.4722		50

and its atomic weight is 50. This estimate is confirmed by the analysis of Robiquet and Colin.

\* Memoirs of the Wernerian Society, vol. i.

† An. de Ch. et de Ph. vol. i. and ii.

The hydrocarburet of chlorine forms a very dense vapour, its specific gravity, according to Gay-Lussac, being 3.4434. This is so near the united densities of chlorine and olefiant gas, as to leave no doubt that the vapour contains its own volume of each of its constituents.

Dr Henry has demonstrated that light is not essential to the action of chlorine on olefiant gas. On this he has founded an ingenious and perfectly efficacious method of separating olefiant gas from light carburetted hydrogen and carbonic oxide gases, neither of which is acted on by chlorine unless light is present. (*Philos. Trans.* for 1821.)

Olefiant gas unites also with iodine. This compound was discovered by Mr Faraday (*Philos. Trans.* for 1821) by exposing olefiant gas and iodine, contained in the same vessel, to the direct rays of the sun. The *hydrocarburet of iodine* is a solid white crystalline body, which has a sweet taste and aromatic odour. It sinks rapidly in strong sulphuric acid. It fuses when heated, and then sublimes without change, condensing into crystals, which are either tabular or prismatic. On exposure to strong heat, it is decomposed, and iodine escapes. It burns, if held in the flame of a spirit lamp, with evolution of iodine and some hydriodic acid. It is insoluble both in water and in acid or alkaline solutions. Alcohol and ether dissolve it, and on evaporating the solution it crystallizes.

The hydrocarburet of iodine is composed according to the analysis of Mr Faraday (*Quarterly Journal of Science*, vol. xiii.) of

Iodine	.	.	124	.	.	or one atom.
Olefiant gas	.	.	14	.	.	or one atom.

M. Serullas has also discovered a compound of olefiant gas and iodine. It has a yellow colour like sulphur, and forms scaly crystals of a pearly lustre. Though it differs from the preceding compound in some of its properties, its composition, according to the analysis of M. Serullas, is precisely analogous. (*Annales de Ch. et de Ph.* vol. xx. and xxii.)

This compound was originally prepared by adding potassium to a solution of iodine in alcohol; but M. Serullas has since made it by mixing a solution of pure potassa in alcohol with an alcoholic solution of iodine. The object of both processes is to present iodine in solution to olefiant gas in a nascent state. It was stated in the section on iodine, that when an alkali, such as potassa, acts on that substance, hydriodic and iodic acids are generated by the decomposition of water. It has been mentioned, also, in the present section, that pure alcohol is a compound of water and olefiant gas. Now, when iodine, potassa, and alcohol, are mixed together, the latter is decomposed:—the water contributes to the formation of iodic and hydriodic acids; while the olefiant gas, instead of assuming the gaseous form, unites with iodine. Potassium acts still more powerfully; because it is converted into potassa at the expense of the water of the alcohol.

### *On the New Carburets of Hydrogen discovered by Mr Faraday.*

In the process of compressing oil gas in Gordon's condensing apparatus, during which the gas is subjected to a force equal to thirty atmospheres, a considerable quantity of liquid collects, which retains its fluidity at the common atmospheric pressure. This liquid, when re-

cently received from the condenser, boils at 60° F. But as soon as the more volatile portions are dissipated, which happens before one-tenth is thrown off, the point of ebullition rises to 100° F.; and the temperature gradually ascends to 250° F. before all the liquid is volatilized. This indicated the presence of several compounds, which differ in their degree of volatility; and Mr Faraday remarked that the boiling point was more constant between 176° and 190° F. than at any other temperature. He was hence led to search for a definite compound in the fluid which came over at that period; and at length by repeated distillations, and exposing the distilled liquid to a temperature of zero, he succeeded in obtaining a substance to which he has applied the term of *bi-carburet of hydrogen*.

The bi-carburet of hydrogen, at common temperatures, is a colourless transparent liquid, which smells like oil gas, and has also a slight odour of almonds. Its specific gravity is nearly 0.85 at 60° F. At 32° F. it congeals, and forms dendritic crystals on the sides of the glass. At zero it is transparent, bitter, and pulverulent, and is nearly as hard as loaf sugar. When exposed to the air at the ordinary temperature it evaporates, and it boils at 186° F. The density of its vapour, at 60° F. and when the barometer stands at 29.93 inches, is nearly 2.7760.

The bi-carburet of hydrogen is very slightly soluble in water, but it dissolves freely in fixed and volatile oils, in ether, and in alcohol, and the alcoholic solution is precipitated by water. It is not acted on by alkalies. It is combustible, and burns with a bright flame and much smoke. When admitted to oxygen gas, so much vapour rises as to make a powerfully detonating mixture. Potassium heated in it does not lose its lustre. On passing its vapour through a red-hot tube, it gradually deposits charcoal, and yields carburetted hydrogen gas. Chlorine, by the aid of sunshine, decomposes it with evolution of muriatic acid. Two triple compounds of chlorine, carbon, and hydrogen, are formed at the same time, one of which is a crystalline solid, and the other a dense thick fluid.

The bi-carburet of hydrogen was analyzed in two ways. In the first, its vapour was passed over oxide of copper heated to redness; and in the second it was detonated with oxygen gas. Carbonic acid and water were the sole products; and as the absence of oxygen is established by the inaction of potassium, it follows that the bi-carburet consists of carbon and hydrogen only. Mr Faraday infers from his analyses, that 100 measures of the inflammable vapour require 750 of oxygen for complete combustion; that 150 measures of oxygen unite with 300 of hydrogen; and that the remaining 600 combine with 600 of the vapour of carbon, forming 600 measures of carbonic acid gas. Consequently, 100 measures of the vapour are composed of

Carbon	. (0.4166×6)	. 2.4996	. 36	. 6 atoms.
Hydrogen	. (0.0694×3)	. 0.2082	. 3	. 3 atoms.

The weight of its atom is therefore 39; and its specific gravity, by calculation, is 2.7078.

The second carburet of hydrogen discovered by Mr Faraday, to which he has not given a name, was derived from the same source as the preceding. It is obtained by heating with the hand the condensed liquid from oil gas, and conducting the vapour which escapes through tubes cooled artificially to zero. A liquid then condenses, which boils



from a slight elevation of temperature, and before the thermometer rises to 32° F. is wholly reconverted into vapour.

This vapour is highly combustible, and burns with a brilliant flame. Its specific gravity, at 60° F. and 29.94 of the barometer, is about 1.9065. On being cooled to zero, it again condenses, and the specific gravity of this liquid at 54° is 0.627; so that among solids and liquids it is the lightest body known.

Water absorbs the vapour sparingly; but alcohol takes it up in large quantity, and the solution effervesces on being diluted with water. Alkalies and muriatic acid do not affect it. Sulphuric acid, on the contrary, absorbs more than 100 times its volume of the vapour. A dark-coloured solution is formed, but no sulphurous acid is disengaged.

From the analysis of this vapour, made by detonating it with oxygen gas, Mr Faraday infers that each volume requires six of oxygen for complete combustion, and yields four volumes of carbonic acid. It hence follows that 100 measures of the vapour contain 400 measures of the vapour of carbon and 400 of hydrogen gas, and that this carburet of hydrogen consists, by weight, of

Carbon	.	(0.4166×4)	.	1.6664	.	21	.	4 atoms.
Hydrogen	.	(0.0694×4)	.	0.2776	.	4	.	4 atoms.

The weight of its atom is therefore 28. Its density must be 1.9440; and Mr Faraday regards this estimate of its specific gravity as nearer the truth than that above stated. The composition of this substance was calculated by Dr Thomson (*Principles of Chemistry*, vol. i. p. 151) before the compound itself had been obtained in an insulated form. He terms it *quadro-carburetted hydrogen*, and is of opinion that it exists in sulphuric ether, combined with one atom of water. This view is justified by the proportion in which the elements of ether are united.

The discovery of this substance has established a fact which is altogether new to chemists. The elements of the new carburet are united in the proportion of 24 to 4, and those of olefiant gas in that of 12 to 2; that is, the carbon and hydrogen in both are in the ratio of 6 to 1, and therefore each may be regarded as a compound of one atom of its component principles. Hence it appears that two substances may be identical with respect to the proportion of their constituents, and yet be quite distinct in their physical and chemical properties.

This peculiarity is explicable on the supposition that the ultimate atoms of such compounds are differently disposed. It is to be presumed that the smallest possible particle of olefiant gas contains two atoms of carbon and two atoms of hydrogen; and that, in like manner, an integrant particle of the new compound of Mr Faraday contains four atoms of each element. Neither of these substances could, I conceive, be formed by direct union of a single atom of carbon and a single atom of hydrogen. If a combination of the kind were to occur, a new compound, different from any known at present, would be the result. Such appears to me the only satisfactory mode of accounting for the phenomena.

### *Naphtha from Coal Tar.*

This substance is obtained by the distillation of coal tar, and is termed *Naphtha* from its similarity to mineral naphtha. It has a strong

and peculiar empyreumatic odour, and is highly inflammable. Potassium may be preserved in it without losing its lustre, which is a sufficient proof that it contains no oxygen. According to Dr Thomson, one measure of the vapour of naphtha contains six measures of the vapour of carbon, and six of hydrogen gas; or, by weight, that it consists of 36 or six atoms of carbon, and 6 or six atoms of hydrogen.

### *Naphthaline.*

This compound is likewise derived from coal tar. If the distillation is conducted at a very gentle heat, the naphtha, from its greater volatility, first passes over; and afterwards the naphthaline rises in vapour, and condenses in the neck of the retort as a white crystalline solid.—(Dr Kid in the Phil. Trans. for 1821\*.)

Pure naphthaline is heavier than water, has a pungent aromatic taste, and a peculiar, faintly aromatic, odour, not unlike that of the narcissus. It is smooth and unctuous to the touch, is perfectly white, and has a silvery lustre. It fuses at  $180^{\circ}$ , and assumes a crystalline texture in cooling. It volatilizes slowly at common temperatures, and boils at  $410^{\circ}$  F. Its vapour, in condensing, crystallizes with remarkable facility in thin transparent laminae.

Naphthaline is not very readily inflamed; but when set on fire it burns rapidly, and emits a large quantity of smoke. It is insoluble in cold, and dissolves very sparingly in hot water. Its proper solvents are alcohol and ether, and especially the latter. Olive oil, the oil of turpentine, and naphtha, likewise dissolve it.

The alkalis do not act upon naphthaline. The acetic and oxalic acids dissolve it, forming pink-coloured solutions. Sulphuric acid enters into direct combination with it, and forms a new and peculiar acid, which Mr Faraday has described in the Philosophical Transactions for 1826, under the name of Sulpho-naphthalic acid.

Naphthaline, according to the analysis of Dr Thomson, is a *sesquicarburet of hydrogen*; that is, a compound of nine or an atom and a half of carbon and one atom of hydrogen. It is desirable, however, that this analysis should be repeated.

### *On Coal and Oil Gas.*

The nature of the inflammable gases derived from the destructive distillation of coal and oil was first ascertained by Dr Henry†, who showed, in several elaborate and able essays, that these gaseous products do not differ essentially from one another, but consist of a few well-known compounds, mixed in different and very variable proportions. The chief constituents were found to be light carburetted hydrogen and olefiant gas, besides which they contain an inflammable vapour, free hydrogen, carbonic acid, carbonic oxide, and nitrogen gases. The discoveries of Mr Faraday have elucidated the subject still farther, by proving that there exists in oil gas, and by inference in coal gas also, the vapour of several definite compounds of carbon and hydrogen, the presence of which, for the purposes of illumination, is exceedingly important.

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\* See also a paper by Mr Brande in the Quarterly Journal of Science, vol. viii.; and Annals of Philosophy, N. S. vol. vi.

† Nicholson's Journal for 1805. Philosophical Transactions for 1808. Ibid. for 1821.

The illuminating power of the ingredients of coal and oil gas is very unequal. Thus the carbonic oxide and carbonic acid are positively hurtful; that is, the other gases would give more light without them.

The nitrogen of course can be of no service. The hydrogen is actually prejudicial; because, though it evolves a large quantity of caloric in burning, it emits an exceedingly feeble light. The carburets of hydrogen are the real illuminating agents, and the degree of light emitted by these is dependent on the quantity of carbon which they contain. Thus olefiant gas illuminates much more powerfully than the light carburetted hydrogen; and, for the same reason, the dense vapour of the quadrocarburet of hydrogen emits a far greater quantity of light, for equal volumes, than the olefiant gas.

From these facts, it is obvious that the comparative illuminating power of different kinds of coal and oil gas may be estimated, approximately at least, by determining the relative quantities of the denser carburets of hydrogen which enter into their composition. This may be done in three ways. 1. By their specific gravity. 2. By the quantity of oxygen required for their complete combustion. 3. By the quantity of gaseous matter condensable by chlorine in the dark; for chlorine, when light is excluded, condenses all the hydro-carburets, excepting the light carburetted hydrogen. Of these methods, the last I conceive is the least exceptionable\*.

The formation of coal and oil gas is a process of considerable delicacy. Coal gas is prepared by heating coal to redness in iron retorts. The quality of the gas, as made at different places or at the same place at different times, is very variable, the density of some specimens having been found so low as 0.443, and that of others so high as 0.700. These differences arise in part from the nature of the coal, and partly from the mode in which the process is conducted. The regulation of the degree of heat is the chief circumstance in the mode of operating, by which the quality of the gas is affected. That the quality of the gas may be influenced by this cause is obvious from the fact, that all the dense hydro-carburets are resolved by a strong red heat either into charcoal and light carburetted hydrogen, or into charcoal and hydrogen. Consequently, the gas made at a very high temperature, though its quantity may be comparatively great, has a low specific gravity, and illuminates feebly. It is therefore an object of importance that the temperature should not be greater than is required for decomposing the coal effectually, and that the retorts be so contrived as to prevent the gas from passing over a red-hot surface subsequently to its formation.

These remarks apply with still greater force to the manufacture of oil gas, because oil is capable of yielding a much larger quantity of the heavy hydrocarburets than coal. The quantity of oil gas from the same material is liable to so great variation from the mode of manufacture, that the density of some specimens has been found so low as 0.464, and that of others so high as 1.110. The average specific gravity of good oil gas is 0.900, and it should never be made higher. The true interest of the manufacturer is to form as much olefiant gas as possible, with only a small proportion of the heavier hydrocarburets. If the lat-

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\* For a discussion of this and other questions relative to oil and coal gas, the reader may consult an essay by Dr Christison and myself in the *Edinburgh Philosophical Journal* for 1825.

ter predominate, the quantity of gas derived from a given weight of oil is greatly diminished; and a subsequent loss is experienced by the condensation of the inflammable vapours when the gas is compressed, or while it is circulating through the distributing tubes.

Coal gas, when first prepared, always contains sulphuretted hydrogen, and for this reason must be purified before being distributed for burning. The process of purification consists in passing the gas under strong pressure through milk of lime, by which means the sulphuretted hydrogen may be entirely removed. But coal gas, after being treated in this manner, still retains some compound of sulphur, most probably, as Mr Brande conjectures, the sulphuret of carbon, owing to the presence of which, sulphurous acid is generated during its combustion. Oil gas, on the contrary, needs no purification; and as it is free from all compounds of sulphur, it yields in burning no sulphurous acid, and is therefore better fitted for lighting dwelling-houses than coal gas.

With respect to the relative economy of the two gases, I may observe that the illuminating power of oil gas, of specific gravity 0.900, is about double that of coal gas of 0.600. In good coal districts, however, oil gas is fully three times the price of coal gas, and therefore in such situations, the latter is considerably cheaper. (Essay above quoted.)

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### SECTION III.

#### COMPOUNDS OF HYDROGEN AND SULPHUR—SULPHURETTED HYDROGEN.

The best method of preparing pure sulphuretted hydrogen is by heating sulphuret of antimony in a retort, or any convenient glass flask, with four or five times its weight of strong muriatic acid. An interchange of elements takes place between water and the sulphuret of antimony, in consequence of which, sulphuretted hydrogen, and the protoxide of antimony, are generated. The former escapes with effervescence, while the latter unites with muriatic acid. The affinities which determine these changes are the attraction of hydrogen for sulphur, of oxygen for antimony, and of muriatic acid for the protoxide of antimony\*.

Sulphuretted hydrogen is also formed by the action of sulphuric or muriatic acid, diluted with three or four parts of water, on the protosulphuret of iron; and the theory of the phenomena is similar to that just mentioned. The protosulphuret of iron may be procured, either by igniting common iron pyrites (the deuto-sulphuret of iron), by which one atom of sulphur is expelled; or by exposing to a low red heat a mixture of two parts of iron filings and rather more than one of sulphur. The materials should be placed in a common earthen or cast iron crucible, and be protected as much as possible from the air

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\* This process may be explained differently. Instead of water, the muriatic acid may be supposed to yield hydrogen to the sulphur, while a chloride of antimony is formed. For reasons, which will afterwards be stated, I adopt the view given in the text.

during the process. The protosulphuret procured from iron filings and sulphur always contains some uncombined iron, and therefore the gas obtained from it is never quite pure, being mixed with a little free hydrogen. This, however, for many purposes, is quite immaterial.

Sulphuretted hydrogen is a colourless gas, and is distinguished from all other gaseous substances by its offensive taste and odour, which is similar to that of putrefying eggs, or the water of sulphurous springs. Under a pressure of 17 atmospheres, at 50° F., it is compressed into a limpid liquid, which resumes the gaseous state as soon as the pressure is removed.

Sulphuretted hydrogen is very injurious to animal life. According to the experiments of Dupuytren and Thénard, the presence of 1-1500th of sulphuretted hydrogen in air, is instantly fatal to a small bird; 1-800th killed a middle sized dog, and a horse died in an atmosphere which contained 1-150th of its volume.

Sulphuretted hydrogen extinguishes all burning bodies; but the gas takes fire when a lighted candle is immersed in it, and burns with a pale blue flame. Water and sulphuric acid are the products of its combustion, and sulphur is deposited. With oxygen gas it forms a mixture which detonates by the application of flame or the electric spark. If 100 measures of sulphuretted hydrogen are exploded with 150 of oxygen, the former is completely consumed, the oxygen disappears, water is deposited, and 100 measures of sulphurous acid gas remain. (Dr Thomson.) From the result of this experiment, the composition of sulphuretted hydrogen may be inferred; for it is clear, from the composition of sulphurous acid, (page 151,) that two-thirds of the oxygen must have combined with sulphur; and, therefore, that the remaining one-third contributed to the formation of water. Consequently, sulphuretted hydrogen contains its own volume of the vapour of sulphur and of hydrogen gas; and since

	<i>Grains.</i>
100 cubic inches of the vapour of sulphur weigh . . .	33.888
100 cubic inches of hydrogen gas weigh . . .	2.118

100 cubic inches of sulphuretted hydrogen gas must weigh 36.006 and its specific gravity is 1.1805.

The accuracy of this estimate is confirmed by several circumstances. Thus, according to Gay-Lussac and Thénard, the weight of 100 cubic inches of sulphuretted hydrogen is 36.33 grains; and Sir H. Davy and Dr Thomson found it somewhat lighter. When sulphur is heated in hydrogen gas, sulphuretted hydrogen is generated without any change of volume. On igniting platinum wires in it by the voltaic apparatus, sulphur is deposited, and an equal volume of pure hydrogen remains. A similar effect is produced, though more slowly, by a succession of electric sparks, (Elements of Sir H. Davy, p. 282.) Gay-Lussac and Thénard have given ample demonstration of the same fact. Thus, on heating tin in sulphuretted hydrogen, a sulphuret of tin is formed; and when potassium is heated in it, a vivid combustion ensues, with formation of the sulphuret of potassium. In both cases, pure hydrogen is left, which occupies precisely the same space as the gas from which it was derived. (*Recherches Physico-Chimiques*, vol. i.)

From the data above stated, it follows that sulphuretted hydrogen is composed, by weight, of



Sulphur	.	33.888	.	16	.	one atom.
Hydrogen	.	2.118	.	1	.	one atom.

Sulphuretted hydrogen has decided acid properties; for it reddens litmus paper, and forms salts with alkalies. It is hence sometimes called *hydro-sulphuric acid*. Its salts are termed *hydro-sulphurets* or *hydro-sulphates*. All the hydro-sulphurets are decomposed by muriatic or sulphuric acid, and sulphuretted hydrogen is disengaged with effervescence.

Recently boiled water absorbs its own volume of sulphuretted hydrogen, and acquires the peculiar taste and odour of sulphurous springs. The gas is expelled without change by boiling.

The elements of sulphuretted hydrogen may easily be separated from one another. Thus, on putting a solution of sulphuretted hydrogen into an open vessel, the oxygen absorbed from the air gradually unites with the hydrogen of the sulphuretted hydrogen, water is formed, and sulphur is deposited. Sulphuretted hydrogen and sulphurous acid mutually decompose each other, with formation of water and deposition of sulphur. If a drachm of fuming nitric acid is poured into a bottle full of sulphuretted hydrogen gas, a bluish-white flame passes rapidly through the vessel, sulphur and nitrous acid fumes make their appearance, and of course water is generated. Chlorine and iodine decompose sulphuretted hydrogen, with separation of sulphur, and formation either of muriatic or hydriodic acid. An atmosphere charged with sulphuretted hydrogen gas may be purified by means of chlorine in the space of a few minutes.

Sulphuretted hydrogen, from its affinity for metallic substances, is a chemical agent of great importance. It tarnishes gold and silver powerfully, forming with them metallic sulphurets. White paint, owing to the lead which it contains, is blackened by it; and the salts of nearly all the common metals are decomposed by its action. In most cases, the hydrogen of the sulphuretted hydrogen combines with the oxygen of the oxide, and the metal unites with the sulphur.

Sulphuretted hydrogen is readily distinguished from other gases by its odour. The most delicate chemical test of its presence is carbonate of lead (white paint) mixed with water and spread upon a piece of white paper. So minute a quantity of sulphuretted hydrogen may by this means be detected, that one measure of the gas mixed with 20,000 times its volume of air, hydrogen, or carburetted hydrogen, gives a brown stain to the whitened surface. (Dr Henry.)

### *Bisulphuretted Hydrogen.*

Though Scheele discovered this compound, it was first particularly described by Berthollet. (*An. de Chimie*, vol. xxv.) It may be made conveniently by boiling equal parts of recently slaked lime and flowers of sulphur with five or six of water, when a deep orange-yellow solution is formed, which contains a hydrosulphuret of lime with excess of sulphur. On pouring this liquid into strong muriatic acid, a copious deposition of sulphur takes place; and the greater part of the sulphuretted hydrogen, instead of escaping with effervescence, is retained by the sulphur. After some minutes, a yellowish semifluid matter like oil collects at the bottom of the vessel, which is *bisulphuretted hydrogen*.

From the facility with which this substance resolves itself into sul-

phur and sulphuretted hydrogen, its history is imperfect, and in some respects obscure. It is viscid to the touch, and has the peculiar odour and taste of sulphuretted hydrogen, though in a slighter degree. It appears to possess the properties of an acid; for it unites with alkalis and the alkaline earths, forming salts which are termed *sulphuretted hydro-sulphurets*. According to Mr Dalton, the bi-sulphuretted hydrogen consists of one atom of hydrogen and two atoms of sulphur; and consequently its combining proportion is 33. This view of its composition is corroborated by Mr Herschel's analysis of the sulphuretted hydrosulphuret of lime. (Edinburgh Philos. Journal, vol. i. p. 13.)

The salts of the bisulphuretted hydrogen may be prepared by digesting sulphur in solutions of the alkaline or earthy hydro-sulphurets. They are also generated when alkalis or alkaline earths are boiled with sulphur and water; but in this case, another salt is formed at the same time. Thus, on boiling together lime and sulphur, as in the preceding process, the only mode by which sulphuretted hydrogen can be formed at all, is by the decomposition of water; but since no oxygen escapes during the ebullition, it is manifest that the elements of that liquid must have combined with separate portions of sulphur, and have formed two distinct acids. One of these, in all probability, is hyposulphurous acid; and the other is sulphuretted hydrogen.

The salts of bisulphuretted hydrogen absorb oxygen from the air, and pass gradually into hyposulphites. A similar change is speedily effected by the action of sulphurous acid. Dilute muriatic and sulphuric acids produce in them a deposition of sulphur, and evolution of sulphuretted hydrogen gas.

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## SECTION IV.

### *HYDROGEN AND SELENIUM—HYDRO-SELENIC ACID.*

Selenium, like sulphur, forms a gaseous compound with hydrogen, which has distinct acid properties, and is termed *seleniuretted hydrogen*, or *hydro-selenic acid*. This gas is disengaged when muriatic acid is added to a concentrated solution of any hydro-seleniate. It may also be procured by heating the seleniuret of iron in muriatic acid. By the decomposition of water, oxide of iron and hydro-selenic acid are generated; and while the former unites with the muriatic acid, the latter escapes in the form of gas.

Hydro-selenic acid gas is colourless. Its odour is at first similar to that of sulphuretted hydrogen; but it afterwards irritates the lining membrane of the nose powerfully, excites catarrhal symptoms, and destroys for some hours the sense of smelling. It is absorbed freely by water, forming a colourless solution, which reddens litmus paper, and gives a brown stain to the skin. The acid is soon decomposed by exposure to the atmosphere, for the oxygen of the air unites with the hydrogen of the hydro-selenic acid, and selenium, in the form of a red powder, subsides.

All the salts of the common metals are decomposed by hydro-selenic

acid. The hydrogen of that acid combines with the oxygen of the oxide, and a seleniuret of the metal is generated.

The hydroselenic acid gas is composed, according to the analysis of Berzelius, of one atom of each of its constituents.

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## SECTION V.

### *HYDROGEN AND PHOSPHORUS—PERPHOSPHURETTED HYDROGEN.*

Perphosphuretted hydrogen was discovered in 1783 by M. Gengembre, and has since been particularly examined by Mr Dalton and Dr Thomson. This gas may be prepared in several ways. The first is by heating phosphorus in a strong solution of pure potassa. The second consists in heating a mixture made of small pieces of phosphorus and recently slaked lime, to which a sufficient quantity of water is added to give it the consistence of a thick paste. The third method is by the action of dilute muriatic acid, aided by a moderate heat, on the phosphuret of lime. In these processes, three compounds of phosphorus are generated;—phosphoric acid, hypo-phosphorous acid, and perphosphuretted hydrogen,—all of which are produced by the decomposition of water, and the combination of its elements with separate portions of phosphorus. The gas should be generated at as low a temperature as possible; for otherwise some free hydrogen is apt to pass over.

Perphosphuretted hydrogen gas has a peculiar odour, resembling that of garlic, and a bitter taste. Its specific gravity, according to Dr Thomson, is 0.9027; and 100 cubic inches at 60° F., and when the barometer stands at 30 inches, weigh 27.5323 grains. Recently boiled water absorbs about 1-50th of its volume, and acquires the peculiar odour of the gas. The solution does not redden litmus paper, nor does the gas itself possess acid properties. The most remarkable property of this compound, by which it is distinguished from all other gases, is the spontaneous combustion which it undergoes on mixing with air or oxygen gas. If the beak of the retort from which it issues is plunged under water, so that successive bubbles of the gas may rise through the liquid, a very beautiful appearance takes place. Each bubble, on reaching the surface of the water, bursts into flame, and forms a ring of dense white smoke, which enlarges as it ascends, and retains its shape, if the air be very tranquil, till it disappears. If the gas is received in a vessel of oxygen gas, the entrance of each bubble is instantly followed by a strong concussion, and a flash of white light of extreme intensity. The products of the combustion in both cases are phosphoric acid and water. Mr Dalton observed that it might be mixed with pure oxygen in a tube of three-tenths of an inch in diameter without taking fire; but the mixture detonates when an electric spark is passed through it.

From the combustibility of phosphuretted hydrogen it would be hazardous to mix it in any quantity with air or oxygen in close vessels. For the same reason, care is required, in making the gas, to allow it to

form very slowly at first, in order that the oxygen within the apparatus may be gradually consumed.

Perphosphuretted hydrogen is resolved into its elements by exposure to a strong heat. The same effect is produced by passing through it a succession of electric sparks, pure hydrogen remaining, which occupies the same space as the gas from which it was derived. When phosphorus is heated in hydrogen gas, some perphosphuretted hydrogen is generated, without any change of volume. (Dr Thomson.) We learn from the same chemist, that if sulphur is heated in perphosphuretted hydrogen, decomposition ensues, and an equal volume of sulphuretted hydrogen results. From these data it follows that perphosphuretted hydrogen contains its own volume of hydrogen. Its composition is therefore determined by subtracting the specific gravity of hydrogen gas from that of perphosphuretted hydrogen. Hence it is composed of

Phosphorus	(0.9027—0.0694)—0.8333	12	one atom.
Hydrogen	0.0694	1	one atom.

and its atomic weight is 13.

When 100 measures of perphosphuretted hydrogen are exploded in a strong tube with an equal volume of oxygen gas, water and phosphorous acid are generated. On the contrary, if 150 measures of oxygen are employed, the products are water and phosphoric acid. (Dr Thomson and Mr Dalton.) In each experiment, 50 measures of oxygen unite with hydrogen, and the remainder with the phosphorus. These are the data from which Dr Thomson infers that the phosphoric contains twice as much oxygen as the phosphorous acid.

### *Protophosphuretted Hydrogen.*

The protophosphuretted hydrogen, discovered in 1812 by Sir H. Davy, is a colourless gas, which has the following properties. Its odour, though disagreeable, is less fetid than that of the preceding compound. Water absorbs about one-eighth of its volume of the gas. It does not take fire when mixed with air or oxygen at common temperatures; but the mixture detonates with the electric spark, or when heated to the temperature of 300° Fahrenheit. Admitted into chlorine gas, it inflames instantly, and emits a white light, a property which it possesses in common with the perphosphuretted hydrogen.

On heating potassium in the protophosphuretted hydrogen, a phosphuret of potassium is formed, and the residue is pure hydrogen, which occupies twice as much space as the gas from which it was derived. When sulphur is heated in 100 measures of this gas, a sulphuret of phosphorus is produced, and 200 measures of sulphuretted hydrogen are obtained. (Sir H. Davy, and Dr Thomson.) Further, Dr Thomson states, that water and sulphurous acid result when 100 measures of the protophosphuretted hydrogen are detonated with 150 of oxygen gas; whereas with 200 of oxygen, the products are water and phosphoric acid. From these data, it follows that the protophosphuretted hydrogen is composed of

Phosphorus	.	12, or one atom.
Hydrogen	.	2, or two atoms.

Its atomic weight is therefore 14. The specific gravity of a gas, so constituted, should be 0.9722.

The protophosphuretted hydrogen is prepared by heating the solid hydrate of phosphorous acid in close vessels. The chemical changes which give rise to its production, are explained by Sir H. Davy in the following manner. (Elements, p. 297.) For every four atoms of phosphorous acid two of water are decomposed. The six atoms of oxygen unite with three of phosphorus, forming three atoms of phosphoric acid; while the remaining atom of phosphorus attaches itself to the two atoms of hydrogen, and forms one atom of protophosphuretted hydrogen.

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## SECTION VI.

### COMPOUNDS OF NITROGEN AND CARBON.

#### *Bicarburet of Nitrogen, or Cyanogen Gas.*

Cyanogen gas, the discovery of which was made in 1815 by M. Gay-Lussac, (Annales de Chimie, vol. xcv.) is prepared by heating the cyanuret of mercury, carefully dried, in a small glass retort by means of a spirit lamp. The cyanuret, which, on the supposition of its being a compound of the oxide of mercury and prussic acid, was formerly called *prussiate of mercury*, is in reality composed of metallic mercury and cyanogen. On exposing it to a low red heat it is resolved into its elements. The cyanogen passes over in the form of gas and the metallic mercury sublimes. The retort, at the close of the process, contains a small residue of charcoal, derived from the cyanogen itself, a portion of which is decomposed by the temperature employed in its formation; but Gay-Lussac states that no free nitrogen is disengaged till towards the close of the process.

Cyanogen gas is colourless, and has a strong pungent and very peculiar odour. At the temperature of 45° F., and under a pressure of 3.6 atmospheres, it is a limpid liquid, which resumes the gaseous form when the pressure is removed. It extinguishes burning bodies; but is inflammable, and burns with a beautiful and characteristic purple flame. It can support a strong heat without decomposition. Water, at the temperature of 60° F., absorbs 4.5 times, and alcohol 23 times, its volume of the gas. The aqueous solution reddens litmus paper; but this effect is not to be ascribed to the gas itself, but to the presence of acids which are generated by the mutual decomposition of cyanogen and water\*.

The composition of cyanogen may be determined by mixing that gas with a due proportion of oxygen, and inflaming the mixture by electricity. Gay-Lussac ascertained in this way that 100 measures of cyanogen require 200 of oxygen for complete combustion, that no water is formed, and that the products are 200 measures of carbonic acid gas and 100 of nitrogen. Hence it follows that cyanogen contains its

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\* Vauquelin, in the Annales de Ch. et de Ph. vol. ix.; or Annals of Philosophy, vol. xiii.



## 208 *Compounds of Nitrogen and Carbon.*

own bulk of nitrogen, and twice its volume of the vapour of carbon. Consequently, since

				Grains.
100 cubic inches of nitrogen gas weigh	.			29.652
200		the vapour of carbon weigh	.	25.418
				<hr/>
100 cubic inches of cyanogen gas must weigh	.			55.070
And it consists by weight of				
Nitrogen	.	29.652	.	14 . one atom.
Carbon	.	25.418	.	12 . two atoms.

The specific gravity of a gas so constituted is 1.8054; whereas Gay-Lussac found it, by weighing, to be 1.8064.

Cyanogen, from this view of its composition, is a *bicarburet* of nitrogen; but for the sake of convenience I shall employ the term *cyanogen*, proposed by its discoverer\*. All the compounds of cyanogen, which are not acid, are called *cyanurets* or *cyanides*.

Cyanogen, though a compound body, has a remarkable tendency to combine with elementary substances. Thus it is capable of uniting with the simple non-metallic bodies, and evinces a strong attraction for metals. When potassium, for instance, is heated in cyanogen, such an energetic action ensues, that the metal becomes incandescent, and a cyanuret of potassium is generated. The affinity of cyanogen for metallic oxides, on the contrary, is comparatively feeble. It enters into direct combination with a few alkaline bases only, and these compounds are by no means permanent. From these remarks it is apparent that cyanogen has no claim to be regarded as an acid.

### *Hydrocyanic or Prussic Acid.*

The Prussic acid was discovered in 1782 by Scheele, and Berthollet afterwards ascertained that it contains carbon, nitrogen, and hydrogen; but Gay-Lussac first procured it in a pure state, and by the discovery of cyanogen was enabled to determine its real nature.

Pure hydrocyanic or prussic acid may be prepared by heating the cyanuret of mercury in a glass retort with two-thirds of its weight of concentrated muriatic acid. By an interchange of elements similar to that which was explained in the first process for forming sulphuretted hydrogen (p. 201), the cyanogen of the cyanuret unites with hydrogen, forming hydrocyanic acid, while a muriate of the peroxide of mercury remains in the retort. The vapour of hydrocyanic acid, as it rises, is mixed with moisture and muriatic acid. It is separated from the latter by being conducted through a narrow tube over fragments of marble, with the lime of which the muriatic acid unites. It is next dried by means of the chloride of calcium, and is subsequently collected in a tube surrounded with ice or snow.

Vauquelin proposes the following process as affording a more abundant product than the preceding. It consists in filling a narrow tube, placed horizontally, with fragments of the cyanuret of mercury, and causing a current of sulphuretted hydrogen gas to pass slowly along it.

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\* From *κυανος* blue, and *γενναω* I generate; because it is an essential ingredient of Prussian blue.

The instant that gas comes in contact with the cyanuret, double decomposition ensues, and hydrocyanic acid and the black sulphuret of mercury are generated. The progress of the sulphuretted hydrogen along the tube may be distinctly traced by the change of colour, and the experiment may be closed as soon as the whole of the cyanuret has become black. It then only remains to expel the hydrocyanic acid by a gentle heat, and collect it in a cool receiver. This process is elegant, easy of execution, and productive.

Pure hydrocyanic acid is a limpid colourless fluid, of a strong odour, similar to that of peach blossoms. It excites at first a sensation of coolness on the tongue, which is soon followed by heat; but when diluted, it has the flavour of bitter almonds. Its specific gravity at 45° F. is 0.7058. It is so exceedingly volatile, that its vapours during warm weather may be collected over mercury. Its point of ebullition is 79° F., and at zero it congeals. When a drop of it is placed on a piece of glass, it becomes solid, because the cold produced by the evaporation of one portion is such as to freeze the remainder. It unites with water and alcohol in every proportion.

Pure hydrocyanic acid is a powerful poison. A single drop of it placed on the tongue of a dog causes death in the course of a very few seconds; and small animals, when confined in its vapour, are rapidly destroyed. On inspiring the vapour, diluted with atmospheric air, headache and giddiness supervene; and for this reason the pure acid should not be made in close apartments during warm weather. The distilled water from the leaves of the *prunus lauro-cerasus* owes its poisonous quality to the presence of this acid.

Pure hydrocyanic acid, even when excluded from air and moisture, is very liable to spontaneous changes, owing to the tendency of its elements to form new combinations. These changes sometimes commence within an hour after the acid is made, and it can rarely be preserved for more than two weeks. The commencement of decomposition is marked by the liquid acquiring a reddish-brown tinge. The colour then gradually deepens, a matter like charcoal subsides, and ammonia is generated. On analyzing the black matter, it was found to contain carbon and nitrogen. The acid may be preserved for a longer period if diluted with water, but even then it undergoes gradual decomposition.

Hydrocyanic acid reddens litmus paper feebly, and unites with most alkaline bases, forming salts which are termed *prussiates* or *hydrocyanates*. It is a weak acid; for it does not decompose the carbonates, and no quantity of it can destroy the alkaline reaction of potassa. Its salts are poisonous; they are all decomposed by carbonic acid, and have the odour of hydrocyanic acid, a character by which the hydrocyanates may easily be recognised.

Hydrocyanic acid is resolved by galvanism into hydrogen and cyanogen, the former of which appears at the negative, and the latter at the positive pole. When its vapour is conducted through a red-hot porcelain tube, partial decomposition ensues. Charcoal is deposited, and nitrogen, hydrogen, and cyanogen gases are set at liberty; but the greater part of the acid passes over unchanged. Electricity produces a similar effect. The vapour of hydrocyanic acid takes fire on the approach of flame; and with oxygen gas it forms a mixture which detonates with the electric spark. The products of the combustion are nitrogen, water, and carbonic acid.

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The composition of hydrocyanic acid is shown by the following simple but decisive experiment of Gay-Lussac. If a quantity of potassium, precisely sufficient for absorbing 50 measures of pure cyanogen gas, is heated in 100 measures of hydrocyanic acid vapour, the cyanuret of potassium is generated, a diminution of 50 measures takes place, and the residue is pure hydrogen. From this it appears that hydrocyanic acid vapour is composed of equal volumes of cyanogen and of hydrogen, united without any condensation; and, consequently, these two gases combine, by weight, according to the ratio of their densities. The composition of hydrocyanic acid may, therefore, be thus stated:—

	<i>By Volume.</i>	<i>By Weight.</i>
Cyanogen	50 . .	1.8054—26, one atom.
Hydrogen	50 . .	0.0694 1, one atom.

100 acid vapour.

The atomic weight of hydrocyanic acid is 27. The specific gravity of its vapour is, of course, the mean of its constituents, or 0.9374; as determined directly by Gay-Lussac its density is 0.9476.

From the powerful action of hydrocyanic acid on the animal economy, this substance, in a diluted form, is sometimes employed medically. It may be procured of any given strength by dissolving the cyanuret of mercury in water, and passing a current of sulphuretted hydrogen gas through the solution till the whole of the cyanuret is decomposed. The excess of sulphuretted hydrogen is removed by agitation with carbonate of lead, and the hydrocyanic acid is then separated from the insoluble matters by filtration. The process adopted at the Apothecaries' Hall, London, is to mix in a retort one part of the cyanuret of mercury, one part of muriatic acid of specific gravity 1.15, and six parts of water; and to distil the mixture. The product has a density of 0.995. (Brande's Manual of Chemistry, vol. i.)

The quality of dilute hydrocyanic acid, however prepared, is very variable, owing to the volatility of the acid, and its tendency to spontaneous decomposition. On this account, it should be made only in small quantities at a time, kept in well-stopped bottles, and excluded from the light. The best way of estimating the strength of any solution is that proposed by Dr Ure. To 100 grains, or any other convenient quantity of the acid, contained in a phial, small quantities of the peroxide of mercury in fine powder are successively added till it ceases to be dissolved. The weight of the peroxide which is dissolved, divided by four, gives the quantity of real hydrocyanic acid present. (Quarterly Journal, vol. xiii.)

The presence of free hydrocyanic acid is easily recognized by its odour. Chemically it may be detected by agitating the fluid supposed to contain it with the oxide of mercury in fine powder. Double decomposition ensues, by which water and the cyanuret of mercury are generated; and on evaporating the solution slowly, the latter is obtained in the form of crystals.

### *Cyanic Acid.*

Chemists are acquainted with two acid compounds of cyanogen and oxygen; and it is remarkable, that though the properties of these acids

are quite different, their elements, according to the best analyses we possess, are united in the same proportion. That two or more different substances may be composed of the same elements combined in the same ratio, is a fact which can hardly be questioned. (Page 198.) But since examples of the kind are as yet exceedingly rare, it will be proper, before admitting the similarity of composition in the present instance, to suspend our judgment till the analysis of the two cyanic acids shall have been repeated and confirmed by other chemists. In the mean time, however, I shall describe each under the term of *cyanic acid*.

*Cyanic acid* of M. Wöhler. It was stated by Gay-Lussac, in the essay already quoted, that cyanogen gas is freely absorbed by pure alkaline solutions; and he expressed the opinion that the alkali combines directly with the cyanogen. It appears, however, from the experiments of M. Wöhler, that, by decomposition of water, hydrocyanic and cyanic acids are formed under these circumstances; and, consequently, that alkaline solutions act upon cyanogen in the same manner as on chlorine, iodine, and sulphur. But the salts of cyanic acid cannot conveniently be procured in this way, owing to the difficulty of separating the cyanate from the hydrocyanate that accompanies it. W. Wöhler finds that the cyanate of potassa may be procured in large quantity by mixing the ferrocyanate of potassa with an equal weight of the peroxide of manganese in fine powder, and exposing the mixture to a low red heat. The cyanogen of the ferrocyanic acid receives oxygen from the manganese, and is converted into cyanic acid, which unites with the potassa. The ignited mass is then boiled in alcohol of 86 per cent.; and as the solution cools, the cyanate is deposited in small tabular crystals like the chlorate of potassa. The only precaution necessary in this process is to avoid too high a temperature.

The cyanic acid is characterized by the facility with which it is resolved by water into carbonic acid and ammonia. This change is effected merely by boiling an aqueous solution of the cyanate of potassa; and it takes place still more rapidly when an attempt is made to decompose the cyanate by means of another acid. If the acid is diluted, the cyanic acid is instantly decomposed, and the carbonic acid escapes with effervescence. But, on the contrary, if a concentrated acid is employed, then the cyanic acid resists decomposition for a short time, and emits a strong odour of vinegar.

The cyanic acid forms a soluble salt with baryta, but insoluble ones with the oxides of lead, mercury, and silver. If the cyanate of potassa is quite pure, it gives a white precipitate with nitrate of silver, and the cyanate of silver so formed dissolves without residue in dilute nitric acid.

Cyanic acid, according to the analysis of M. Wöhler, is composed of 26 parts or one atom of cyanogen, and 8 parts or one atom of oxygen. (*Annales de Chimie et de Physique*, vol. xx. and xxvii.) M. Liebig has attempted to prove that cyanic acid consists of one atom of cyanogen and half an atom of oxygen; and contends that it should be called *cyanous acid*; but M. Wöhler has repeated his own analysis, and confirmed his former result.

The existence of cyanic acid was suspected by M. Vauquelin before it was actually discovered by Wöhler. The experiments of the former chemist led him to the opinion that a solution of cyanogen in water is gradually converted into hydrocyanic, cyanic, and carbonic acids, and ammonia; and he supposed alkalies to produce a similar

change. He did not establish the fact, however, in a satisfactory manner. (An. de Ch. et de Ph. vol. ix.)

*Cyanic acid* of M. Liebig. A powerfully detonating compound of mercury was described in the Philosophical Transactions for 1800 by Mr E. Howard. It is prepared by dissolving 100 grains of mercury in a measured ounce and a half of nitric acid of specific gravity 1.3; and adding, when the solution has become cold, two ounces by measure of alcohol, the density of which is 0.849. The mixture is then heated till a moderately brisk effervescence takes place, during which the fulminating compound is generated. A similar substance may be made by treating silver in the same manner. The conditions necessary for forming these compounds are, that the silver or mercury be dissolved in a fluid which contains so much free nitric acid and alcohol, that, on the application of heat, nitric ether shall be freely disengaged.

Fulminating silver and mercury bear the heat of  $212^{\circ}$  or even of  $260^{\circ}$  F. without detonating; but a higher temperature, or slight percussion between two hard bodies, causes them to explode with violence. The nature of these compounds was discovered in 1823 by M. Liebig\*, who demonstrated that they are salts composed of a peculiar acid, which he termed *fulminic acid*, in combination with the oxide of mercury or of silver. According to an analysis of fulminating silver made by MM. Liebig and Gay-Lussac†, the acid of the salt is composed of 26 parts or one atom of cyanogen, and 8 parts or one atom of oxygen. It is therefore a real *cyanic acid*, and its salts may with propriety be termed *cyanates*. The fulminating silver is a cyanate of the oxide of silver; and is found to contain one atom of each element.

It is remarkable that the oxide of silver cannot be entirely separated from cyanic acid by means of an alkali. On digesting the cyanate of silver in potassa, for example, one atom of the oxide of silver is separated, and a double cyanate is formed, which consists of two atoms of cyanic acid, one atom of the oxide of silver, and one atom of potassa. Similar compounds may be procured by substituting other alkaline substances, such as baryta, lime or magnesia, for the potassa. These double cyanates are capable of crystallizing; and they all possess detonating properties.

From the presence of the oxide of silver in the double cyanates, it was at first imagined that this oxide actually constitutes a part of the acid; but since several other substances, such as the oxides of mercury, zinc, and copper, may be substituted for that of silver, this view can no longer be admitted.

The cyanic acid has not hitherto been obtained in an insulated form; for while some acids do not decompose the cyanates, others act on the cyanic acid itself, and give rise to new products. Muriatic acid, for example, causes the formation of hydrocyanic acid, and a new acid containing chlorine, carbon and nitrogen, the nature of which has not been determined. Hydriodic acid acts in a similar manner; and a peculiar acid is likewise produced by the action of sulphuretted hydrogen.

\* Ann. de Ch. et de Ph. vol. xxiv.

† Ibid. xxv.



*Chlorocyanic Acid.*

When chlorine gas is conducted into an aqueous solution of hydrocyanic acid till the liquid acquires bleaching properties, and the excess of chlorine is then removed by agitation with mercury, two acids are obtained, one of which is the muriatic acid, and the other a compound of cyanogen and chlorine. The existence of this acid was first noticed by Berthollet, who called it *oxy-prussic acid*, on the supposition of its containing prussic acid and oxygen; but Gay-Lussac, having determined its real composition, proposed the more appropriate term of *chloro-cyanic acid*.

The chlorocyanic acid has not hitherto been procured in a separate state. When first formed, it is mixed with muriatic acid and water; and on heating the solution, a gas is expelled which may be collected over mercury, and which, on examination, is found to be a mixture of chlorocyanic and carbonic acids. The presence of carbonic acid gas is owing to the circumstance that the heat employed to expel the chlorocyanic acid, excites reaction between the elements of that gas and of water, in consequence of which muriatic acid, ammonia, and carbonic acid are generated.

It is not known with certainty whether pure chlorocyanic acid, at the common temperature and pressure, is liquid or gaseous. When mixed with carbonic acid, it is a colourless gas, which has a strong pungent odour, and excites a flow of tears. It is not inflammable, nor does it form an explosive mixture with oxygen, unless a little hydrogen is added. It is absorbed by water, and forms with it a liquid which reddens litmus paper, and which does not give a precipitate either with nitrate of silver or with solution of pure baryta. It combines with alkalies, without decomposition; but when an acid is added, brisk effervescence ensues, owing to the evolution of carbonic acid.—Gay-Lussac has proved, that the chlorocyanic acid, at the moment of being separated from an alkali, reacts upon water, and thus gives rise to the same change as is produced on its aqueous solution by heat.

According to the analysis of M. Gay-Lussac, chlorocyanic acid gas is composed of equal volumes of chlorine and cyanogen gases, united without any condensation; or, by weight, of

Chlorine	.	36	.	one atom.
Cyanogen	.	26	.	one atom.

The weight of its atom is therefore 62, and its density in the gaseous state must be 2.1527.

*Cyanogen and Iodine.*

The *cyanuret of iodine*, which was discovered in 1824, by M. Serullas, (*An. de Ch. et de Ph.* vol. xxvii.) may be prepared by the following process:—Two parts of the cyanuret of mercury and one of iodine, quite dry, are intimately and quickly mixed in a glass mortar, and the mixture is introduced into a phial with a wide mouth. On applying heat, the violet vapours of iodine appear; but as soon as the cyanuret of mercury begins to be decomposed, the vapour of iodine is succeeded by white fumes, which, if received in a cool glass receiver, condense upon its sides into flocks like cotton wool.

The cyanuret of iodine, when slowly condensed, occurs in very long and exceedingly slender needles, of a white colour. It has a very caustic taste and penetrating odour, and excites a flow of tears. It sinks rapidly in sulphuric acid. It is very volatile, and sustains a temperature much higher than  $212^{\circ}$  F. without decomposition; but is decomposed by a red heat. It dissolves in water and alcohol, and forms solutions which do not redden litmus paper.

The cyanuret of iodine is decomposed by a concentrated solution of potassa with formation of hydriodic and hydrocyanic acids. As these compounds could only have been formed by the decomposition of water, the solution ought also to contain the iodic and cyanic acids; but M. Serullas did not succeed in detecting their presence.

The sulphurous acid, when water is present, has a very powerful action on the cyanuret of iodine. On adding a few drops of this acid, iodine is set free, and hydrocyanic acid is produced; but when more of the sulphurous acid is employed, the iodine disappears, and the solution is found to contain hydriodic acid. These changes are of course accompanied with the formation of sulphuric acid, and the decomposition of water.

The cyanuret of iodine has not been analyzed with accuracy; but M. Serullas infers, from an approximative analysis, that it is composed of one atom of iodine and one atom of cyanogen.

### *Ferrocyanic Acid.*

The ferrocyanic acid has, within these few years, been the subject of able researches by Mr Porrett\*, Berzelius†, and M. Robiquet‡. Mr Porrett recommends two methods for obtaining the ferrocyanic acid, by one of which it is procured in crystals, and by the other in a state of solution. The first process consists in dissolving 58 grains of crystallized tartaric acid in alcohol, and mixing the liquid with 50 grains of the ferrocyanate of potassa dissolved in the smallest possible quantity of hot water. The bitartrate of potassa is precipitated, and the clear solution, on being allowed to evaporate spontaneously, gradually deposits ferrocyanic acid in the form of small cubic crystals of a yellow colour. In the second process, the ferrocyanate of baryta, dissolved in water, is mixed with a quantity of sulphuric acid, which is precisely sufficient for combining with the baryta. The insoluble sulphate of baryta subsides, and the ferrocyanic acid remains in solution. According to Mr Porrett, every ten grains of the ferrocyanate of baryta require so much liquid sulphuric acid as is equivalent to 2.53 grains of real acid.

The ferrocyanic acid is neither volatile nor poisonous in small quantities, and has no odour. It is gradually decomposed by exposure to the light, forming hydrocyanic acid and Prussian blue; but it is far less liable to spontaneous decomposition than the hydrocyanic acid. It differs also from this acid by possessing the properties of acidity in a much greater degree. Thus it reddens litmus paper permanently, neutralizes alkalies, and separates the carbonic and acetic acids from

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\* Philosophical Transactions for 1814 and 1815. *Annals of Philosophy*, vol. xiv.

† *Annales de Chimie et de Physique*, vol. xv.

‡ *Ibid.* vol. xvii.

their combinations. It even decomposes some salts of the more powerful acids. The peroxide of iron, for example, unites with the ferrocyanic in preference to the sulphuric acid, unless the latter is concentrated.

Different opinions have prevailed as to the nature of ferrocyanic acid. Berzelius maintains that it is a super-hydrocyanate of the protoxide of iron; but M. Robiquet has shown by arguments which appear to me unanswerable, that this supposition is inconsistent with the phenomena. The view which is now commonly taken of the composition of this acid, was suggested by an experiment made by Mr Porrett. On exposing the ferrocyanate of soda to the agency of galvanism, the soda was observed to collect at the negative pole, while oxide of iron, together with the elements of hydrocyanic acid, appeared at the opposite end of the battery. From this he inferred, that the iron does not act the part of an alkali in the salt, for on that supposition it should have accompanied the soda, but that it enters into the constitution of the acid itself. Mr Porrett at first considered the iron to be in the state of an oxide; but he concludes from subsequent researches, that the ferrocyanic acid contains no oxygen, and that its sole elements are carbon, hydrogen, nitrogen, and metallic iron. To the acid thus constituted, he proposes the name of *ferruretted chyazic\* acid*; but the term *ferro-cyanic acid*, introduced by the French chemists, is more generally employed.

This view has the merit of accounting for the fact, that iron, though contained in ferrocyanic acid and all its salts, cannot be detected in them by the usual tests of iron. For the liquid tests are fitted only for detecting the oxide of iron as existing in a salt, and therefore cannot be expected to indicate the presence of metallic iron while forming one of the elements of an acid. We may now also understand how it happens that the ferrocyanic should actually contain the elements of hydrocyanic acid, and yet differ from it totally in its properties.

According to the experiments of Mr Porrett, the ferrocyanic acid is composed of one atom of iron, one atom of hydrocyanic acid, and two atoms of carbon. M. Robiquet states however, that its elements are in such proportion as to form cyanuret of iron, and hydrocyanic acid; and the result of his researches, together with the analysis of Berzelius, appears to justify the conclusion that the ferrocyanic acid is composed of

Hydrogen	.	.	.	.	2 atoms.
Iron	.	.	.	.	1 atom.
Cyanogen	.	.	.	.	3 atoms.
or of					
Hydrocyanic acid	.	.	.	.	2 atoms.
Cyanuret of iron	.	.	.	.	1 atom†.

The ferrocyanic acid is, therefore, analogous to several acids, such as the muriatic, hydriodic, and hydrosulphuric acids, all of which contain hydrogen as an essential element, and which for this reason are termed *hydracids*. Under this point of view, the ferrocyanic acid may

\* *Chyazic* from the initials of carbon, hydrogen, and azote.

† See a notice on the Triple Prussiates in the *An. de Ch. et de Ph.* vol. xxii.

be regarded as a compound of a certain *radical* and hydrogen. This radical, which has not been obtained in an insulated state, is composed of

Cyanogen	.	3 atoms.	} or of	Cyanogen	.	2 atoms.
Iron	.	1 atom.		Cyanuret of iron	.	1 atom.

and the acid itself consists of one atom of the radical and two atoms of hydrogen.

The salts of ferrocyanic acid were once called *triple prussiates*, on the supposition that they are composed of prussic or hydrocyanic acid, in combination with the oxide of iron and some other alkaline base. They are now termed *ferrocyanates*. The beautiful dye, Prussian blue, is a ferrocyanate of the peroxide of iron. It is always formed when ferrocyanic acid or its salts are mixed in solution with a per-salt of iron; and for this reason the per-salts of iron, provided no free alkali is present, afford a certain and an extremely delicate test of the presence of ferrocyanic acid.

### *Sulphocyanic Acid.*

The sulphocyanic acid was discovered in 1808 by Mr Porrett, who ascertained that it is a compound of sulphur, carbon, hydrogen, and nitrogen, and described it under the name of *sulphuretted chyzic acid*. It is now more commonly called *sulpho-cyanic acid*, and its salts are termed *sulpho-cyanates*.

The sulphocyanic acid is obtained by mixing so much sulphuric acid with a concentrated solution of the sulpho-cyanate of potassa as is sufficient to neutralize the alkali, and then distilling the mixture. An acid liquor collects in the recipient, which is sulphocyanic acid dissolved in water, and the sulphate of potassa remains in the retort.

The sulphocyanic acid, as thus prepared, is a transparent liquid, which is either colourless or has a slight shade of pink. Its odour is somewhat similar to that of vinegar. The strongest solution of it which Mr Porrett could obtain had a specific gravity of 1.022. It boils at 216.5° F.; and at 54.5° F. crystallizes in six-sided prisms.

The sulphocyanic acid reddens litmus paper, and forms neutral compounds with alkalis. Its presence, whether free or combined, is easily detected by a per-salt of iron, with the oxide of which it unites, forming a soluble salt of a deep blood-red colour. With the protoxide of copper it yields a white salt, which is insoluble in water.

According to the analysis of Mr Porrett, (*Annals of Philosophy*, vol. xiii.) which is confirmed by that of Berzelius, (*An. de Ch. et de Ph.* vol. xvi.) the sulphocyanic acid is composed of

Cyanogen	.	26	.	one atom.
Sulphur	..	32	.	two atoms.
Hydrogen	.	1	.	one atom.
or of				
Bisulphuret of cyanogen		58	.	or one atom.
Hydrogen	.	1	.	or one atom.

The sulphocyanic acid is, therefore, a hydracid; and though its radical, the bisulphuret of cyanogen, has not been obtained in a separate state, it is capable, like the radicals of all the other hydracids, of combining with metallic substances.

Berzelius also succeeded in proving the existence of a *selenio-cy-*

*anic acid*, though he could not separate it from its combination with potassa. It is likewise a hydracid, and its radical is a seleniuret of cyanogen.

## SECTION VII.

### COMPOUNDS OF SULPHUR.

#### *Bisulphuret of Carbon.*

This substance was discovered accidentally in 1796 by Professor Lampadius, who regarded it as a compound of sulphur and hydrogen, and termed it *alcohol of sulphur*. Clément and Desormes first declared it to be a sulphuret of carbon, and their statement was fully confirmed by the joint researches of Berzelius and the late Dr Marcet. (Philos. Trans. for 1813.)

The sulphuret of carbon may be obtained by heating in close vessels the native bisulphuret of iron (iron pyrites) with one-fifth of its weight of well-dried charcoal; or by passing the vapour of sulphur over fragments of charcoal heated to redness in a tube of porcelain. The compound, as it forms, should be conducted by means of a glass tube into cold water, at the bottom of which it is collected. To free it from moisture and adhering sulphur, it should be distilled at a low temperature in contact with the chloride of calcium.

The bisulphuret of carbon is a transparent colourless liquid, which is remarkable for its high refractive power. Its specific gravity is 1.272. It has an acrid, pungent, and somewhat aromatic taste, and a very fetid odour. It is exceedingly volatile;—its vapour at 63°.5 F. supports a column of mercury, 7.36 inches long; and at 110° F. it enters into brisk ebullition. From its great volatility it may be employed for producing an intense degree of cold.

The bisulphuret of carbon is very inflammable, and kindles in the open air at a temperature scarcely exceeding that at which mercury boils. It burns with a pale blue flame. Admitted into a vessel of oxygen gas, so much vapour rises as to form an explosive mixture. It dissolves readily in alcohol and ether, and is precipitated from the solution by water. It dissolves phosphorus and iodine, and the solution of the latter has a beautiful pink colour. Chlorine decomposes it, with formation of the chloride of sulphur. The pure acids have little action upon it. With the alkalies it unites slowly, forming compounds which Berzelius calls *carbo-sulphurets*. It is converted by strong nitro-muriatic acid into a white crystalline substance like camphor, which Berzelius considers to be a compound of muriatic, carbonic, and sulphurous acid gases.

*Xanthogen and Hydroxanthic acid.*—M. Zeise, Professor of chemistry in Copenhagen, has lately discovered some novel and interesting facts, relative to the bisulphuret of carbon. When this fluid is agitated with a solution of pure potassa in strong alcohol, the alkaline properties of the potassa disappear entirely; and on exposing the solution to a temperature of 32° F. numerous acicular crystals are deposit-



ed. M. Zeise attributes these phenomena to the formation of a new acid, the elements of which are derived, in his opinion, partly from the alcohol, and partly from the bisulphuret of carbon. He regards the acid as a compound of carbon, sulphur and hydrogen. He supposes it to be a hydracid, and that its radical is a sulphuret of carbon. To the radical of this hydracid he applies the term *Xanthogen*, (from *ξανθος* *yellow*, and *γενναω* *I generate*,) expressive of the fact that its combinations with several metals have a yellow colour. The acid itself is called *hydroxanthic acid*, and its salts *hydroxanthates*. The crystals deposited from the alcoholic solution are the hydroxanthate of potassa.

There is no doubt of a new acid being generated under the circumstances described by M. Zeise; but since he has not procured xanthogen in an insulated form, nor even determined with certainty the constituent principles of the hydroxanthic acid, there exists considerable uncertainty as to its real nature. On this account I refer the reader to the original essay for more ample details concerning it. (An. de Ch. et de Ph. vol. xxi.; and Annals of Philosophy, N. S. vol. iv.)

*Sulphuret of Phosphorus*.—When sulphur is brought into contact with fused phosphorus, they unite readily, but in proportions which have not been precisely determined; and they frequently react on each other with such violence as to cause an explosion. For this reason the experiment should be made with a quantity of phosphorus not exceeding thirty or forty grains. The phosphorus is placed in a glass tube, five or six inches long, and about half an inch wide, and when by a gentle heat it is liquefied, the sulphur is added to it in successive small portions. Caloric is evolved at the moment of combination, and sulphuretted hydrogen and phosphoric acid, owing to the presence of moisture, are generated. This compound may also be made by agitating the flowers of sulphur with fused phosphorus under water. The temperature should not exceed 160° F.; for otherwise sulphuretted hydrogen and phosphoric acid would be evolved so freely as to prove dangerous, or at least to interfere with the success of the process.

The sulphuret of phosphorus, from the nature of its elements, is highly combustible. It is much more fusible than phosphorus. A compound made by Mr Faraday, with about five parts of sulphur to seven of phosphorus, was quite fluid at 32° F., and did not solidify at 20° F. (Quarterly Journal, vol. iv.)

## SECTION VIII.

### COMPOUNDS OF SELENIUM.

#### *Sulphuret of Selenium.*

When sulphuretted hydrogen gas is conducted into a solution of selenic acid, an orange-coloured precipitate subsides, which is a sulphuret of selenium. It fuses at a heat a little above 212° F., and at a still higher temperature may be sublimed without change. In the open air it takes fire when heated, and sulphurous, selenious, and selenic acids

are the products of its combustion. The alkalies and alkaline hydro-sulphurets dissolve it. Nitric acid acts upon it with difficulty; but nitro-muriatic acid converts it into sulphuric and selenic acids. (*Annals of Philosophy*, vol. xiv.) According to Berzelius, this sulphuret is composed of

Selenium	.	40	.	one atom.
Sulphur	.	24	.	one atom and a half.

Selenium and sulphur combine readily by the aid of heat, but it is difficult in this way to obtain a definite compound.

### *Phosphuret of Selenium.*

The phosphuret of selenium may be prepared in the same manner as the sulphuret of phosphorus; but as selenium is capable of uniting with phosphorus in several proportions, the compound formed by fusing them together can hardly be supposed to be of a definite nature. This phosphuret is very fusible, sublimes without change in close vessels, and is inflammable. It decomposes water gradually when digested in it, giving rise to seleniuretted hydrogen, and one of the acids of phosphorus. (*Annals of Philosophy*, vol. xiv.)

# METALS.

## GENERAL PROPERTIES OF METALS.

**METALS** are distinguished from other substances by the following properties. They are all conductors of electricity and caloric. When combined with oxygen, chlorine, iodine, or sulphur, and the resulting compounds are submitted to the action of galvanism, the metals always appear at the negative side of the battery, and for this reason are said to be positive electrics. They are quite opaque, refusing a passage to light, though reduced to very thin leaves. They are in general good reflectors of light, and possess a peculiar lustre, which is termed the metallic lustre.—Every substance in which these characters reside may be regarded as a metal.

The number of metals, the existence of which is admitted by chemists, amounts to forty. The following table contains the names of those that have been procured in a state of purity, together with the date at which they were discovered, and the names of the chemists by whom the discovery was made.

*Table of the Discovery of Metals.*

<i>Names of Metals.</i>	<i>Authors of the Discovery.</i>	<i>Dates of the Discovery.</i>
Gold . . .	} Known to the Ancients .	
Silver . . .		
Iron . . .		
Copper . . .		
Mercury . . .		
Lead . . .		
Tin . . .	} Described by Basil Valentine	15th century
Antimony . . .		
Zinc . . .	Described by Agricola in .	1520
Bismuth . . .	First mentioned by Paracelsus	16th century
Arsenic . . .	} Brandt in . . . . .	1733
Cobalt . . .		
Platinum . . .	Wood, Assay Master, Jamaica	1741
Nickel . . .	Cronstedt . . . . .	1751
Manganese . . .	Gahn and Scheele . . . . .	1774
Tungsten . . .	M. M. D'Elhuyart . . . . .	1781
Tellurium . . .	Müller . . . . .	1782
Molybdenum . . .	Hielm . . . . .	1782

<i>Names of Metals.</i>	<i>Authors of the Discovery.</i>	<i>Dates of the Discovery.</i>
Uranium . . .	Klaproth . . .	1789
Titanium . . .	Gregor . . .	1791
Chromium . . .	Vauquelin . . .	1797
Columbium . . .	Hatchett . . .	1802
Palladium . . .	} Dr Wollaston . . .	1803
Rhodium . . .		
Iridium . . .	Descotils and Smithson Tennant . . .	1803
Osmium . . .	Smithson Tennant . . .	1803
Cerium . . .	Hisinger and Berzelius . . .	1804
Potassium . . .	} Sir H. Davy . . .	1807
Sodium . . .		
Barium . . .		
Strontium . . .		
Calcium . . .	} Stromeyer . . .	1818
Cadmium . . .		
Lithium . . .	Arfwedson . . .	1818
Silicium . . .	} Berzelius . . .	1824
Zirconium . . .		

Most of the metals are remarkable for their great specific gravity, some of them, such as gold and platinum, which are the densest known bodies in nature, being more than nineteen times heavier than an equal bulk of water. Great density was once supposed to be an essential character of metals; but the discovery of potassium and sodium, which are so light as to float on the surface of water, has shown that this supposition is erroneous. Some metals experience an increase of density to a certain extent when hammered, their particles being permanently approximated by the operation. On this account the specific gravity of some of the metals contained in the following table, is represented as varying between two extremes:—

*Table of the Specific Gravity of Metals, at 60° Fahr. compared to water as unity.*

Platinum . . .	20.98 . . .	Brisson
Gold . . .	19.257 . . .	Do.
Tungsten . . .	17.6 . . .	D'Elhuyart
Mercury . . .	13.568 . . .	Brisson
Palladium . . .	11.3 to 11.8 . . .	Wollaston
Lead . . .	11.352 . . .	Brisson
Silver . . .	10.474 . . .	Do.
Bismuth . . .	9.822 . . .	Do.
Uranium . . .	9.000 . . .	Bucholz
Copper . . .	8.895 . . .	Hatchett
Cadmium . . .	8.604 . . .	Stromeyer
Cobalt . . .	8.538 . . .	Haüy
Arsenic . . .	8.308 . . .	Bergmann
Nickel . . .	8.279 . . .	Richter
Iron . . .	7.788 . . .	Brisson
Molybdenum . . .	7.400 . . .	Hielm
Tin . . .	7.291 . . .	Brisson
Zinc . . .	6.861 to 7.1 . . .	Do.

Manganese	.	.	6.850	.	.	Bergmann
Antimony	.	.	6.702	.	.	Brisson
Tellurium	.	.	6.115	.	.	Klaproth
Titanium	.	.	5.3	.	.	Wollaston
Cerium	.	.	4.489 to 4.619			{ Hisinger and
Sodium	.	.	0.972	}	.	{ Berzelius
Potassium	.	.	0.865	}	.	{ Gay-Lussac
						{ and Thénard.

Some metals possess the property of *malleability*, that is, admit of being beaten into thin plates or leaves by hammering. The malleable metals are gold, silver, copper, tin, platinum, palladium, cadmium, lead, zinc, iron, nickel, potassium, sodium, and frozen mercury. The other metals are either malleable in a very small degree only, or, like antimony, arsenic, and bismuth, are actually brittle. Gold surpasses all metals in malleability:—one grain of it may be extended so as to cover about 52 square inches of surface, and to have a thickness not exceeding 1-282020th of an inch.

Nearly all malleable metals may be drawn out into wires, a property which is expressed by the term *ductility*. The only metals which are remarkable in this respect are gold, silver, platinum, iron, and copper. Dr Wollaston has described a method by which gold wire may be obtained so fine that its diameter shall be only 1-5000th of an inch, and that 550 feet of it are required to weigh one grain. He has obtained a platinum wire so small, that its diameter did not exceed 1-30,000th of an inch. (Philos. Transactions for 1813.) It is singular that the ductility and malleability of the same metal are not always in proportion to one another. Iron, for example, cannot be made into fine leaves, but it may be drawn into very small wires.

The tenacity of metals is measured by ascertaining the greatest weight which a wire of a certain thickness can support, without breaking. According to the experiments of Guyton-Morveau, whose results are comprised in the following table, iron, in point of tenacity, surpasses all other metals.

The diameter of each wire was 0.787th of a line.

					<i>Pounds.</i>
Iron wire supports	.	.	.	.	549.25
Copper	.	.	.	.	302.278
Platinum	.	.	.	.	274.32
Silver	.	.	.	.	187.137
Gold	.	.	.	.	150.753
Zinc	.	.	.	.	109.54
Tin	.	.	.	.	34.63
Lead	.	.	.	.	27.621

The metals differ also in hardness, but I am not aware that their exact relation to one another, under this point of view, has been determined by experiment. In the list of hard metals may be placed titanium, manganese, iron, nickel, copper, zinc, and palladium. Gold, silver, and platinum are softer than these; lead is softer still, and potassium and sodium yield to the pressure of the fingers. The properties of elasticity and sonorousness are allied to that of hardness. Iron and copper are in these respects the most conspicuous.

Many of the metals have a distinctly crystalline texture. Iron, for example, is fibrous; and zinc, bismuth, and antimony, are lamellated.



Metals are sometimes obtained also in crystals; and when they do crystallize, they always assume the figure of a cube, the regular octahedron, or some form allied to it. Gold, silver, and copper occur naturally in crystals, while others crystallize when they pass gradually from the liquid to the solid condition. Crystals are most readily procured from those metals which fuse at a low temperature; and bismuth, from conducting caloric less perfectly than other metals, and therefore cooling more slowly, is best fitted for the purpose. The process should be conducted in the way already described for forming crystals of sulphur. (Page 149.)

The metals, with the exception of mercury, are solid at common temperatures; but they may all be liquefied by heat. The degree at which they *fuse*, or their *point of fusion*, is very different for different metals, as will appear by inspecting the following table. (Thénard's Chemistry, vol. i.)

*Table of the fusibility of different Metals.*

		<i>Fahr.</i>	
<i>Fusible below a red heat.</i>	Mercury . . . .	—39°	Different Chemists.
	Potassium . . . .	136	Gay-Lussac and
	Sodium . . . .	190	Thénard.
	Tin . . . .	430	Newton.
	Bismuth . . . .	493	
	Lead . . . .	500	Biot.
	Tellurium—rather less fusible than lead . . . .		Klaproth.
	Arsenic—undetermined.		
	Zinc . . . .	698	Brongniart.
	Antimony—a little below a red heat.		
	Cadmium . . . .		Stromeyer.

*Pyrometer of Wedgwood.*

<i>Infusible below a red heat.</i>	Silver . . . .	20°	Kennedy.
	Copper . . . .	27	Wedgwood.
	Gold . . . .	32	
	Cobalt—rather less fusible than iron.		
	Iron . . . .	{ 130	Wedgwood.
		{ 158	Mackenzie.
	Manganese . . . .	160	Guyton.
	Nickel—the same as Manganese . . . .		Richter.
	Palladium.		
	Molybdenum	{ Almost infusible, and not to be procured in buttons by the heat of a smith's forge.	{ Fusible before the oxygen blow-pipe.
	Uranium		
	Tungsten		
	Chromium		
	Titanium	{ Infusible in the heat of a smith's forge, but fusible before the oxygen blow-pipe.	
	Cerium		
	Osmium		
	Iridium		
	Rhodium		
	Platinum		
	Columbium		

The metals differ also in volatility. Some are readily volatilized by caloric, while others are of so fixed a nature that they may be exposed to the most intense heat of a wind furnace without being dissipated in vapour. There are seven metals the volatility of which has been ascertained with certainty; namely, cadmium, mercury, arsenic, tellurium, potassium, sodium and zinc.

The metals cannot be resolved into more simple parts, and therefore, in the present state of chemistry, they must be regarded as elementary bodies. It was formerly conceived that they might be converted into one another; and this notion led to the vain attempts of the alchemists to convert the baser metals into gold. The chemist has now learned that his sole art consists in resolving compound bodies into their elements, and causing substances to unite which were previously uncombined. There is not a single fact in support of the opinion that one elementary principle can assume the properties peculiar to another.

Metals have an extensive range of affinity, and on this account few of them are found in the earth *native*, that is, in an uncombined form. They commonly occur in combination with other bodies, especially with oxygen and sulphur, in which state they are said to be *mineralized*. It is a singular fact in the chemical history of the metals that they are little disposed to combine in the metallic state with compound bodies. Chemists are not acquainted with any instance of a metal combining either with a metallic oxide or with an acid. They unite readily, on the contrary, with elementary substances. Thus, under favourable circumstances, they combine with one another, forming compounds termed *alloys*, which possess all the characteristic properties of the pure metals. They unite likewise with the simple substances not metallic, such as oxygen, chlorine, and sulphur, giving rise to new bodies in which the metallic character is wholly wanting. In all these combinations the same tendency to unite in a few definite proportions is conspicuous as in that department of the science of which I have just completed the description. The chemical changes are regulated by the same general laws, and in describing them the same nomenclature is applicable.

The method which I propose to adopt in treating the metallic bodies has already been explained in the introduction. Before proceeding, however, to describe the metals individually, I shall make some general observations by which the study of this subject will be much facilitated.

Metals are of a combustible nature, that is, they are not only susceptible of slow oxidation, but, under favourable circumstances, they unite rapidly with oxygen, giving rise to all the phenomena of real combustion. Zinc burns with a brilliant flame when heated to full redness in the open air; iron emits vivid scintillations on being inflamed in an atmosphere of oxygen gas; and the least oxidable metals, such as gold and platinum, scintillate in a similar manner when heated by the oxy-hydrogen blow-pipe.

The product either of the slow or rapid oxidation of a metal, when heated in the air, has an earthy aspect, and was called a *calx* by the older chemists, the process of forming it being expressed by the term *calcination*. Another method of oxidizing metals is by *deflagration*; that is, by mixing them with the nitrate or chlorate of potassa, and projecting the mixture into a red-hot crucible. Most metals may be

oxidized by digestion in nitric acid; and nitro-muriatic acid is an oxidizing agent of still greater power.

Some metals unite with oxygen in one proportion only, but most of them have two or three degrees of oxidation. Metals differ remarkably in their relative forces of attraction for oxygen. Potassium and sodium, for example, are oxidized by mere exposure to the air; and they decompose water at all temperatures the instant they come in contact with it. Iron and copper may be preserved in dry air without change, nor can they decompose water at common temperatures; but they are both slowly oxidized by exposure to a moist atmosphere, and combine rapidly with oxygen when heated to redness in the open air. Iron has a stronger affinity for oxygen than copper; for the former decomposes water at a red heat, whereas the latter cannot produce that effect. Mercury is less inclined to unite with oxygen than copper. Thus it may be exposed without change to the influence of a moist atmosphere. At a temperature of  $650^{\circ}$  or  $700^{\circ}$  F. it is oxidized; but at a red heat it is reduced to the metallic state, while the oxide of copper can sustain the strongest heat of a blast furnace without losing its oxygen. The affinity of silver is still weaker than that of mercury for oxygen; for it cannot be oxidized by the sole agency of caloric at any temperature.

Metallic oxides suffer *reduction*, or may be *reduced* to the metallic state in several ways:

1. By heat alone. By this method the oxides of gold, silver, mercury, and platinum, may be decomposed.

2. By the united agency of heat and combustible matter. Thus, by conducting a current of hydrogen gas over the oxides of copper or of iron heated to redness in a tube of porcelain, water is generated, and the metals are obtained in a pure form. Carbonaceous matters are likewise used for the purpose with great success. Potassa and soda, for example, may be decomposed by exposing them to a white heat after being intimately mixed with charcoal in fine powder. A similar process is employed in metallurgy for procuring the metals from their ores, the inflammable materials being wood, charcoal, coke, or coal. In the more delicate operations of the laboratory, charcoal and the *black flux* are preferred.

3. By the galvanic battery. This is a still more powerful agent than the preceding; since some oxides, such as baryta and strontia, which resist the united influence of heat and charcoal, are reduced by the agency of galvanism.

4. By the action of deoxidizing agents on metallic solutions. The phosphorous acid, for example, when added to a liquid containing the oxide of mercury, deprives the oxide of its oxygen, metallic mercury subsides, and phosphoric acid is generated. In like manner, one metal may be precipitated by another, provided the affinity of the latter for oxygen exceeds that of the former. Thus, when mercury is added to a solution of the nitrate of the oxide of silver, metallic silver is thrown down, and oxide of mercury is dissolved by the nitric acid. On placing metallic copper in the liquid, pure mercury subsides, and a nitrate of the oxide of copper is formed; and from this solution metallic copper may be precipitated by means of iron.

Metals, like the simple non-metallic bodies, may give rise to oxides or acids by combining with oxygen. The former are the most frequent products. Many metals form oxides, which are not acidified by oxygen; whereas one metal only, arsenic, is capable of forming an

acid and not an oxide. All the other metals which are convertible into acids by oxygen, such as chromium, tungsten, and molybdenum, are also susceptible of yielding one or more oxides. In these instances, the acids always contain a larger quantity of oxygen than the oxides of the same metal.

The distinguishing feature of the metallic oxides is the property possessed by many of them of entering into combination with acids. All salts, those of ammonia excepted, are composed of an acid and a metallic oxide. In some instances all the oxides of the same metal are capable of forming salts with acids, as is exemplified by the oxides of iron. More commonly, however, the protoxide is the sole *alkaline* or *salifiable base*. Most of the metallic oxides are insoluble in water; but all those that are soluble have the property of giving a brown stain to the yellow turmeric paper, and of restoring the blue colour of reddened litmus.

Chlorine has a powerful affinity for metallic substances. It combines readily with most metals at common temperatures, and the action is in many instances so violent as to be accompanied with the evolution of light. For example, when powdered zinc, arsenic, or antimony, is thrown into a jar of chlorine gas, the metal is instantly inflamed. The attraction of chlorine even surpasses that of oxygen for metals. Thus, when chlorine is brought into contact at a red heat with pure lime, magnesia, baryta, strontia, potassa, or soda, oxygen is emitted, and a chloride of the metal is generated, the elements of which are so strongly united, that no temperature hitherto tried can separate them. All other metallic oxides are, with few exceptions, acted on in the same manner by chlorine, and in some cases the change takes place below ignition.

All the metallic chlorides are solid at the common temperature, except the bichlorides of tin and of arsenic, which are liquid. They are fusible by heat, assume a crystalline texture in cooling, and, under favourable circumstances, crystallize with regularity. Several of them, such as the chlorides of tin, arsenic, antimony, and mercury, are volatile, and may be sublimed without change. They are for the most part colourless, do not possess the metallic lustre, and have the aspect of salt. Two of the chlorides are insoluble in water, namely the chloride of silver and the protochloride of mercury:—the others are affected by that fluid in a way which will shortly be considered.

Two only of the metallic chlorides, those namely of gold and platinum, are decomposable by heat. All the chlorides of the common metals are decomposed at a red heat by hydrogen gas, muriatic acid being disengaged while the metal is set free. Pure charcoal does not effect their decomposition; but if moisture be present at the same time, muriatic and carbonic acid gases are formed, and the metal remains.

Chlorine manifests a feeble affinity for metallic oxides. No combination of the kind can occur at a red heat, and no chloride of a metallic oxide can be heated to redness without decomposition. Such compounds can only be formed at low temperatures; and they are possessed of little permanency. It is well known that chlorine may combine, under favourable circumstances, with the alkalies and alkaline earths; and Mr Grouvelle has succeeded in making it unite with magnesia, and the oxides of zinc, copper, and iron. (*An. de Ch. et de*

Ph. vol. xvii.) Of these chlorides, that of potassa may be taken as an example. If chlorine is conducted into a dilute and cold solution of pure potassa, the chloride of that alkali will be produced; but the affinity which gives rise to its formation is not sufficient for rendering it permanent. It is destroyed by most substances that act on either of its constituents. Thus, the addition of an acid has this effect by combining with the alkali, and hence the carbonic acid of the air tends to decompose it. Animal or vegetable colouring matters are fatal to it, by giving chlorine an opportunity to exert its bleaching power; and, indeed, the colour is removed by the chloride of potassa as readily as by a solution of chlorine in pure water. It is also destroyed by the action of heat; nor can its solution be concentrated without decomposition; for, in either case, the muriatic and chloric acids are generated. (P. 165.)

Iodine has a strong attraction for metals; and most of the compounds it forms with them sustain a red heat in close vessels without decomposition. But in the degree of its affinity for metallic substances it is inferior both to chlorine and oxygen. We have seen that chlorine has a stronger affinity for metals than oxygen, since it decomposes nearly all oxides at high temperatures; and it separates iodine also from metals under the same circumstances. If the vapour of iodine is brought into contact with potassa, soda, protoxide of lead, or the oxide of bismuth, heated to redness, oxygen gas is evolved, and an iodide of these metals will be formed. But iodine, so far as is known, cannot separate oxygen from any other metal; nay, all the iodides, except those just mentioned, are decomposed by exposure to oxygen gas at the temperature of ignition.

When the vapour of iodine is conducted over red-hot lime, baryta, or strontia, oxygen is not disengaged, but an iodide of those oxides, according to Gay-Lussac, is generated. The iodides of these oxides are therefore more permanent than the analogous compounds with chlorine. Iodine does not combine with any other oxide under the same circumstances; and indeed all other such iodides, very few of which exist, are, like the chlorides of oxides, possessed of little permanency, and are decomposed by a red heat.

The action of iodine on metallic oxides, when dissolved or suspended in water, is precisely analogous to that of chlorine. On adding iodine to a solution of the pure alkalis or alkaline earths, water is decomposed, and the hydriodic and iodic acids are generated.

Sulphur, like chlorine and iodine, has a strong tendency to unite with metals. The combination may be effected in several ways:

1. By heating the metal directly with sulphur. The metal, in the form of powder or filings, is mixed with a due proportion of sulphur, and the mixture is then heated in an earthen crucible, which is covered to prevent the access of air. Or if the metal can sustain a red heat without fusing, the vapour of sulphur may be passed over it while heated to redness, in a tube of porcelain. The act of combination, which frequently ensues below the temperature of ignition, is attended by a free disengagement of caloric; and in several instances the heat evolved is so great, that the whole mass becomes luminous, and shines with a vivid light. This appearance of combustion, which occurs quite independently of the presence of oxygen, is exemplified by the sulphurets of potassium, sodium, copper, iron, lead, and bismuth.



2. By igniting a mixture of a metallic oxide and sulphur. The sulphurets of the common metals may be made by this process. The elements of the oxide unite with separate portions of sulphur, forming sulphurous acid gas, which is disengaged, and a metallic sulphuret which remains in the retort.

3. By depriving the sulphate of an oxide of its oxygen by means of heat and combustible matter. Charcoal or hydrogen gas may be employed for the purpose, as will be described immediately.

4. By sulphuretted hydrogen, or an alkaline hydrosulphuret. Nearly all the salts of the common metals are decomposed when a current of sulphuretted hydrogen gas is conducted into their solutions. The salts of uranium, iron, manganese, cobalt, and nickel, are well known exceptions; but these also are precipitated by the hydrosulphuret of ammonia or potassa.

The sulphurets are opaque brittle solids, many of which, such as the sulphurets of lead, antimony, and iron, have a metallic lustre. They are all fusible by heat, and commonly assume a crystalline texture in cooling. Most of them are fixed in the fire; but the sulphurets of mercury and arsenic are remarkable for their volatility. All the sulphurets, excepting those which are formed of the metallic bases of the alkalies and earths, are insoluble in water.

Most of the protosulphurets are capable of supporting an intense heat without decomposition; but those which contain more than one atom of sulphur, lose a part of it when strongly heated. They are all decomposed without exception by exposure to the combined agency of heat and air or oxygen gas; and the products depend entirely on the degree of heat and the nature of the metal. The sulphuret is converted into the sulphate of an oxide, provided the sulphate is able to support the temperature employed in the operation. If this is not the case, then the sulphur is evolved under the form of sulphurous acid, and a metallic oxide is left; or if the oxide itself is decomposed by heat, the pure metal remains. The action of heat and air in decomposing metallic sulphurets is the basis of several metallurgic processes.

Many of the metallic sulphurets were formerly believed to be compounds of sulphur and a metallic oxide; and I believe this was first shown to be an error by Proust in the essays which he published in the *Journal de Physique*. In the 53d volume of that work, he demonstrated that the sulphuret of iron, (magnetic pyrites,) as well as the common cubic pyrites or bisulphuret, are compounds of sulphur and metallic iron without any oxygen. He showed the same also with respect to the sulphurets of other metals, such as those of mercury and copper. He was of opinion, however, that in some instances sulphur does unite with a metallic oxide. Thus, when sulphur and the peroxide of tin are heated together, sulphurous acid is disengaged, and the residue according to Proust is a sulphuret of the protoxide.

It was the general belief at that time, also, that the compounds formed by heating sulphur with an alkali or earth are sulphurets of a metallic oxide. Thus, the old *hepar sulphuris*, the *sulphuretum potassæ* of the Edinburgh Pharmacopœia, which is made by fusing together a mixture of sulphur and dry carbonate of potassa, was regarded as a sulphuret of potassa. In the year 1817 M. Vauquelin published an essay in the 6th volume of the *Annales de Chimie et de Physique*, wherein he detailed some experiments, the object of which was to de-

termine the state of the alkali in that compound. The late Count Berthollet had observed that when the *hepar sulphuris* is dissolved in water, the solution always contains a considerable portion of sulphuric acid, which he conceived to be generated at the moment of solution. He supposed that water is then decomposed; and that its elements combine with different portions of sulphur, the oxygen giving rise to the formation of sulphuric acid, and the hydrogen to sulphuretted hydrogen. The accuracy of this explanation was called in question by Vauquelin in the paper above mentioned, who contended that the sulphuric acid is generated, not during the process of solution, but by the action of heat during the formation of the sulphuret. One portion of potassa, according to him, yields its oxygen at a high temperature to some of the sulphur, converting it into sulphuric acid, while the potassium unites with pure sulphur. Two combinations therefore result—sulphuret of potassium and sulphate of potassa, which are mixed together. Though the experiments adduced in favour of this opinion were not absolutely convincing, yet they made it the more probable of the two; and M. Vauquelin, admitting however the want of actual proof, inferred from them that when an alkaline oxide is heated to redness with sulphur, the former loses oxygen, and a sulphuret of the metal itself is produced.

The sixth volume of the *Annals* likewise contains a paper by M. Gay-Lussac, who offered additional arguments in favour of Vauquelin's opinion, and I believe most chemists held them to be satisfactory. But the more recent labours of MM. Berthier and Berzelius have given still greater insight into the nature of these compounds. One of Vauquelin's chief arguments was drawn from the action of charcoal on the sulphate of potassa. When a mixture of this salt with powdered charcoal is ignited without exposure to the air, carbonic oxide and carbonic acid gases are formed, and a sulphuret is left, analogous both in appearance and properties to that which may be made by igniting carbonate of potassa directly with sulphur. They are both essentially the same substance, and Vauquelin conceived, from the strong attraction of carbon for oxygen, that both the sulphuric acid and the potassa would be decomposed by charcoal at a high temperature; and that, consequently, the product must be a sulphuret of potassium.

M. Berthier has proved in the following manner that these changes do actually occur. (*An. de Ch. et de Ph.* vol. xvii.) He put a known weight of sulphate of baryta into a crucible lined with a mixture of clay and charcoal, defended it from contact with the air, and exposed it to a white heat for the space of two hours. By this treatment it suffered complete decomposition, and it was found that in passing into a sulphuret, it had suffered a loss in weight precisely equal to the quantity of oxygen originally contained in the acid and earth. This circumstance, coupled with the fact that there had been no loss of sulphur, is decisive evidence that the baryta as well as the acid had lost its oxygen, and that a sulphuret of barium had been formed. He obtained the same results also with the sulphates of strontia, lime, potassa, and soda; but from the fusibility of the sulphurets of potassium and sodium, their loss of weight could not be determined with such precision as in the other instances.

The experiments of Berzelius, performed about the same time, are exceedingly elegant, and still more satisfactory than the foregoing. (*An. de Ch. et de Ph.* vol. xx.) He passed a stream of dry hydrogen gas over a known quantity of sulphate of potassa, heated to redness.

It was expected from the strong affinity of hydrogen for oxygen, that the sulphate would be decomposed; and, accordingly, a considerable quantity of water was formed, which was carefully collected and weighed. The loss of weight which the salt had experienced, was precisely equivalent to the oxygen of the acid and alkali; and the oxygen of the water was exactly equal to the loss in weight. A similar result was obtained with the sulphates of soda, baryta, strontia, and lime.

It is demonstrated, therefore, that the metallic bases of the alkalies and alkaline earths agree with the common metals in their disposition to unite with sulphur. It is now certain that, whether we decompose a sulphate by hydrogen or charcoal, or whether we ignite sulphur with an alkali or an alkaline earth, a metallic sulphuret is always the product. Direct combination between sulphur and a metallic oxide is a rare occurrence, and it may be almost doubted if it ever happens. Gay-Lussac indeed states that, when an alkali or an alkaline earth is heated with sulphur in such a manner that the temperature is never so high as a low red heat, the product is really the sulphuret of an oxide. But the facts adduced in favour of this opinion are not altogether satisfactory, and we must leave it therefore to be decided by future observation.

Several of the metallic sulphurets occur abundantly in nature. Those that are most frequently met with, are the sulphurets of lead, antimony, copper, iron, zinc, molybdenum, and silver.

The metallic seleniurets have so close a resemblance in their chemical relations to the sulphurets, that it is unnecessary to give a separate description of them. They may be prepared either by bringing selenium in contact with the metals at a high temperature, or by the action of hydro-selenic acid on metallic solutions.

Cyanogen, as already mentioned (page 208,) has an affinity for metallic substances. Few of the cyanurets, however, have been hitherto obtained in a separate state, excepting those of potassium, mercury, silver, and palladium. The three latter are readily decomposed by a red heat.

Cyanogen unites also with some of the metallic oxides. When hydrocyanic acid vapour is passed over pure baryta contained in a porcelain tube, and heated till it begins to be luminous, hydrogen gas is evolved, and cyanuret of baryta, according to Gay-Lussac, is generated. The same chemist succeeded in forming the cyanurets of potassa and soda by a similar process. These compounds exist only in the dry state. A change is produced in them by the action of water, the nature of which has already been explained. (Page 211.)

One subject remains respecting the compounds of chlorine, iodine, sulphur, selenium, and cyanogen with metals, the consideration of which I have hitherto delayed, because it applies to all of them equally. The non-metallic ingredient of each of these compounds is the radical of a hydracid, that is, it has the property of forming with hydrogen an acid, which, like other acids, is unable to unite with metals, but which combines readily with metallic oxides. Owing to this circumstance, a difficulty arises in explaining what takes place when such substances are dissolved in water. Thus, when the chloride, sulphuret, and cyanuret of potassium are put into water, it is possible that they may

dissolve in that liquid without suffering any other chemical change, so that the solution actually contains the chloride, sulphuret, and cyanuret of potassium. It may be supposed, on the other hand, however, that when either of them, for example the chloride of potassium, is put into water, a portion of that liquid is decomposed; the hydrogen unites with the chlorine, forming muriatic acid, and the oxygen with the potassium, converting it into potassa, and consequently the solution must contain a neutral muriate of potassa. Of course, had the sulphuret and cyanuret of potassium been employed, hydrosulphuret and hydrocyanate of potassa might in like manner have been generated. It would be easy to determine which opinion is correct, could it be ascertained whether water is or is not decomposed during the process of solution. But this is the precise point of difficulty; since, from the operation of the laws of definite proportion, no evolution of gas does or can occur to indicate any such change. Still, however, there are circumstances which appear to prove that water must have been decomposed. Thus, on adding sulphuric acid to a concentrated solution of the chloride of potassium, sulphate of potassa is formed, and muriatic acid gas is disengaged. The formation of sulphuretted hydrogen, while water is acting on the sulphuret of potassium, may be inferred from the odour of the solution; and accordingly that gas is actually disengaged on the addition of some stronger acid. Again, that the cyanuret of potassium is converted into hydrocyanate of potassa by water, is manifest from the odour and taste of the solution. It does not indeed follow, because muriatic acid and sulphuretted hydrogen gases are evolved at the moment of adding an acid, that they previously existed as such in the liquid; for the same phenomena would occur on adding sulphuric acid to the dry chloride and sulphuret of potassium. The proof of the cyanuret of potassium being converted by water into the hydrocyanate of potassa appears, on the contrary, quite satisfactory; and it will throw some light on the question, to consider the affinities which must have determined the change. The affinity of oxygen for hydrogen, and that of cyanogen for potassium, are the quiescent affinities which oppose the decomposition of water; the divellent affinities are the attraction of cyanogen for hydrogen, of potassium for oxygen, and of hydrocyanic acid for potassa. The latter prevail; and it follows, *a fortiori*, that the chloride of potassium would be liable to a similar change, because the affinity of chlorine for hydrogen, and of muriatic acid for potassa, is incomparably greater than that of cyanogen and hydrocyanic acid for the same substances.

A similar process of reasoning, aided by the close analogy existing among this class of bodies, has induced most chemists to adopt the opinion, that the compounds of potassium with the radicals of the hydracids in general, uniformly decompose water at the moment of dissolving in that fluid. This view must of course be extended to all such compounds as contain any metal which, like potassium, has a strong attraction for oxygen, and will therefore include the metallic bases of the earths and alkalis. Thus the chloride and iodide of sodium, calcium, and barium, are regarded as the muriates and hydriodates of soda, lime and baryta, when dissolved in water. Some chemists are even disposed to extend the same doctrine to the compounds of every metal with the radical of the hydracids, with the view of comprising every instance within one general law.

But as the circumstances are so very variable, it may be doubted if any single rule can apply to every case. The conditions which



may be expected to influence the result are two-fold: the attraction of the radical of the hydracid for hydrogen and the affinity of the metal for oxygen. A difference in the first circumstance alone does not appear very important, since, if the preceding observations are correct, both the chloride and cyanuret of potassium occasion the decomposition of water. The effect of the second is probably of more importance. We should expect from the difference between potassium and gold in relation to oxygen, that the chloride of potassium would decompose water more easily than the chloride of gold; and there is ground for believing that the latter does really dissolve without any change. For M. Pelletier has shown that the oxide of gold performs the function of an acid rather than of a saline base, since it actually combines with alkalis, but forms no permanent combination with any acid which contains oxygen. This being the case, it is difficult to conceive how the oxide of gold should have so strong an attraction for muriatic acid;—it is most probably a chloride even while in solution. If this be true, then we must infer that the cyanuret and iodide of gold do not decompose water; because, while the metal is the same, cyanogen and iodine have a less affinity for hydrogen than chlorine.

If these remarks are well founded, it follows that the second condition, or the affinity of the metal for oxygen, has the most influence over the decomposition of water: and if any rules may be given, they should be founded chiefly on that circumstance. The decomposition of water may be predicted when the metallic base of the alkalis or earths are in combination with the radical of any hydracid. It may also be expected when iron, zinc, manganese, or tin are present,—metals which decompose water by aid of the strong acids. Accordingly we find that when the chloride of iron is put into water, the solution has the usual colour of the salts of iron, confirming the supposition that the muriate of the oxide had been formed. With respect to such metals as copper, lead, cobalt, &c., the affinity of which for oxygen is less energetic than that of the metals above mentioned, the greater number of the compounds which they form with the radicals of the hydracids decompose water during the act of solution. Thus the chlorides of copper, cobalt, and nickel, instantly acquire, when put into water, the characteristic colour of the salts of those metals. It is very doubtful, on the contrary, whether the chloride of lead occasions a similar change. The few metals, the oxides of which are reduced at a red heat, such as mercury, silver, gold, platinum, &c., have, generally speaking, a strong affinity for the radicals of the hydracids, and to all appearance the compounds so constituted cannot decompose water. It is very questionable whether the oxides of mercury, silver, gold, and platinum, can unite at all with muriatic acid.

It should be remembered, however, that the action of re-agents on the solution of a chloride is generally the same as if it was in reality a muriate. Thus, when potassa is added to a solution of the chloride of gold, a solution of muriate of potassa is obtained, and the oxide of gold separates, water being decomposed at the moment of adding the alkali. The same happens in the case of a solid chloride; a solution of potassa or lime water separates the protoxide of mercury from the chloride of mercury or calomel; and, in like manner, sulphuric acid disengages muriatic acid from the chloride of sodium. For all practical purposes, therefore, the solution of a metallic chloride in water may be viewed as the muriate of an oxide; and on this account I shall always regard it as such in the present treatise.



A similar view may be applied to the solutions of metallic iodides, sulphurets and cyanurets. Whatever may be their nature when dissolved in water, the action of reagents upon them is the same as if they were real salts. To this remark, the cyanuret of mercury is an exception. This compound has every appearance of dissolving in water without change.

Berzelius is of opinion that all soluble metallic chlorides, iodides, and the like, dissolve as such in water, and that salts of the hydracids have no existence. This doctrine, however, appears to me quite inadmissible; for, independently of the foregoing remarks, with which it is inconsistent, its inaccuracy may, I conceive, be shown in the following manner.—I have stated (page 180) that when potassa acts on iodine, the iodic and hydriodic acids are generated by the decomposition of water, and the solution therefore contains the iodate and hydriodate of that alkali. According to Berzelius, on the contrary, the liquid contains the iodate of potassa and the iodide of potassium. Now, the only consistent mode of accounting for their formation is, that iodic acid derives its oxygen, not from water, but from the potassa, and that the potassium unites directly with the iodine. On this supposition, water is not decomposed at all; whereas it is demonstrable that it does undergo decomposition.—The process for forming the hydrocarburet of iodine, employed by M. Serullas, affords decisive proof that water is decomposed during the mutual action of iodine and potassa. (Page 196.)

Having explained what generally happens when the compounds of metals with the radicals of the hydracids are put into water, I may add a few words on the changes which take place when they are separated from that fluid by evaporation. No salt, the acid of which is a hydracid, can sustain a red heat without decomposition; for the oxygen of the oxide and the hydrogen of the acid, being in the proportion for forming water, unite together, and are expelled as watery vapour. A temperature considerably below ignition, is commonly sufficient to produce the same change; nay, it frequently happens during the mere act of crystallization. Thus, when the solution of the muriate of potassa and of soda is gradually evaporated, crystals are deposited, which contain neither oxygen nor hydrogen, and can therefore be nothing but the chlorides of potassium and sodium. It hence follows, that a real muriate of potassa, or of soda, exists only in solution, and that they cease to be salts when they assume the solid form. This circumstance was formerly considered so strange, that it was even adduced as an argument against the existence of chlorine as a simple body. The singularity of the case was, however, only apparent, and arose from ignorance of certain compounds with which we are now acquainted. A salt is a compound of some acid with a metallic oxide or with ammonia, and such was presumed to be the nature of common sea salt and prussiate of mercury; but since the former has been proved to consist of chlorine and sodium, and the latter of cyanogen and mercury, they of course cease to fall under the definition of a salt, though, like the salts, they assume a regular crystalline form.

It appears very improbable to beginners at first sight, that water should be so frequently decomposed and reproduced without any direct proof of it; but if we reflect on a few familiar phenomena, all surprise will cease. During the action of dilute sulphuric acid on iron, a most complex chemical operation ensues, of which we in reality see nothing. The elements of water are dissolved, the oxygen unites with

the iron, the oxide of iron with the sulphuric acid, and the sulphate of the oxide of iron is dissolved by the water; all this is one momentary event, unaccompanied by any visible sign. Again, when dilute sulphuric acid acts on the sulphuret of iron, the same takes place as in the preceding instance, with the additional circumstance that sulphur and hydrogen combine. The escape of hydrogen in the first example, and of sulphuretted hydrogen in the second, is a mechanical phenomenon not necessarily connected with the chemical actions we have just considered; may, were hydrogen and sulphuretted hydrogen colourless limpid fluids like water, we should in reality see no motion whatever during the process; and yet the presence of the oxide of iron, the sulphuric acid having suffered no change, would have afforded abundant proof of the decomposition of water. Other examples might be brought forward of a similar nature, but these are quite sufficient for the purpose.

Chemists are acquainted with several metallic phosphurets; and it is probable that phosphorus, like sulphur, is capable of uniting with all the metals. Little attention however has hitherto been devoted to their compounds; and for the greater part of our knowledge concerning them we are indebted to the researches of Pelletier. (*An. de Chimie*, vol. i. and xiii.)

The metallic phosphurets may be prepared in several ways. The most direct method is by bringing phosphorus in contact with metals at a high temperature, or what amounts to the same thing, by igniting metals in contact with phosphoric acid and charcoal. Many of the phosphurets may be formed by passing a current of phosphuretted hydrogen gas over metallic oxides heated to redness in a porcelain tube. Water is generated, and a phosphuret of the metal remains.

Phosphorus unites also with some of the metallic oxides. The phosphurets of lime and baryta, for example, may be made by conducting the vapour of phosphorus over those earths at a red heat.

The only metallic carburets of importance are those of iron, which will be described in the section on that metal.

Hydrogen unites with few metals. The only metallic hydrogurets known are those of zinc, potassium, arsenic, and tellurium. No compound of nitrogen and a metal has hitherto been discovered.

As the number of the metals is considerable, it is necessary to facilitate the study of them as much as possible by arrangement. The order in which I shall arrange them is similar to that introduced by M. Thénard, and since adopted with a slight modification by Dr Henry in his "*Elements of Experimental Chemistry*." The metals are accordingly divided into the two following classes:—

CLASS I. Metals, the oxides of which cannot be reduced to the metallic state by the sole action of heat.

CLASS II. Metals, the oxides of which are reducible by heat only.

CLASS I. The metals of the first class were formerly called *base* or *imperfect* metals, in contradistinction to gold, silver, and mercury, which were termed the *noble* or *perfect* metals. As the metals contained in the first class are numerous, and differ from one another in the degree of their affinity for oxygen, they may be subdivided into four orders.

Order 1. Metals which decompose water at common temperatures. These are six in number; namely,

Potassium  
Sodium

Lithium  
Barium

Strontium  
Calcium.

The protoxides of the first three metals are distinguished by their causticity and solubility in water, and by possessing alkaline properties in an eminent degree. They are called *alkalies*, and their metallic bases are frequently termed the *alkaline metals*. The protoxides of barium, strontium, and calcium, are commonly denominated *alkaline earths*; because, though they have the acrid taste and alkaline reaction of the pure alkalies, they approach, both in their appearance and in their sparing solubility in water, to the nature of the earths.

The metals of this order are sometimes called *metalloids*, an incorrect expression introduced by the unphilosophical ideas at one time entertained on the conditions requisite to constitute a metal, and which may now be abandoned. A body either does or does not possess the essential properties of a metal. If it does possess them, it is to all intents and purposes a real metal.

Order 2. Metals, which are supposed to be analogous to the foregoing, but the exact nature of which has not been determined. They are six in number; namely,

Magnesia  
Glucinum

Yttrium  
Aluminum

Zirconium  
Silicium.

The oxides of these metals have a white colour and an earthy aspect, and are very sparingly soluble in water. They are called *earths*, and their metallic bases are sometimes called *earthy metals*.

Order 3. Metals which decompose water at a red heat. They are five in number; namely,

Manganese,  
Zinc,

Iron,  
Tin,

Cadmium.

Order 4. Metals which do not decompose water at any temperature. Of these there are fifteen in number; namely,

Arsenic,  
Molybdenum,  
Chromium,  
Tungsten,  
Antimony,

Uranium,  
Columbium,  
Nickel,  
Cobalt,  
Cerium,

Titanium,  
Bismuth,  
Copper,  
Tellurium,  
Lead.

CLASS II. The second class comprises only eight metals, the oxides of which are decomposed by a red heat. These are

Mercury,  
Silver,  
Gold,

Platinum,  
Palladium  
Rhodium,

Osmium,  
Iridium.

## SECTION I.

### POTASSIUM.

Potassium was discovered in 1807 by Sir H. Davy, and the circumstances which led to the discovery have already been described. (Page 68.) It was prepared by that philosopher by causing the hy-

drate of potassa, slightly moistened for the purpose of increasing its conducting power, to communicate with the opposite poles of a galvanic battery of 200 double plates; when the oxygen both of the water and the potassa passed over to the positive pole, while the hydrogen of the former, and the potassium of the latter, made their appearance at the negative wire. By this process potassium is obtained in small quantity only; but Gay-Lussac and Thénard invented a method by which a more abundant supply of it may be procured. (*Recherches Physico-Chimiques*, vol. i.) Their process consists in bringing fused hydrate of potassa in contact with turnings of iron heated to whiteness in a gun-barrel. The iron, under these circumstances, deprives the water and potassa of oxygen, hydrogen gas combined with a little potassium is evolved, and pure potassium sublimes, and may be collected in a cool part of the apparatus.

Potassium may also be prepared, as first noticed by M. Curaudau, by mixing dry carbonate of potassa with half its weight of powdered charcoal, and exposing the mixture, contained in a gun-barrel or spheroidal iron bottle, to a strong heat. An improvement on both processes has been made by M. Brunner, who decomposes potassa by means of iron and charcoal. From eight ounces of fused carbonate of potassa, six ounces of iron filings, and two ounces of charcoal, mixed intimately and heated in an iron bottle, he obtained 140 grains of potassium. (*Quarterly Journal*, vol. xv.) Berzelius has observed that the potassium thus made, though fit for all the usual purposes for which it is required, contains a minute quantity of carbon.

Potassium is solid at the ordinary temperature of the atmosphere. At 70° F. it is somewhat fluid, though its fluidity is not perfect till it is heated to 150° F. At 50° F. it is soft and malleable, and yields like wax to the pressure of the fingers; but it becomes brittle when cooled to 32° F. It sublimes at a red heat without undergoing any change, provided the atmospheric air be completely excluded. Its texture is crystalline, as may be seen by breaking it across while brittle. In colour and lustre it is precisely similar to mercury. At 60° F. its density is 0.865, so that it is considerably lighter than water. It is quite opaque, and is a good conductor of electricity and caloric.

The most prominent chemical property of potassium is its affinity for oxygen gas. It oxidizes rapidly in the air, or by contact with fluids which contain oxygen. On this account it must be preserved either in glass tubes hermetically sealed, or under the surface of liquids, such as naphtha, of which oxygen is not an element. If heated in the open air, it takes fire, and burns with a white flame and great evolution of caloric. It decomposes water on the instant of touching it, and so much heat is disengaged, that the potassium is inflamed, and burns vividly while swimming upon its surface. The hydrogen unites with a little potassium at the moment of separation; and this compound takes fire as it escapes, and thus augments the brilliancy of the combustion. When potassium is plunged under water, violent re-action ensues, but without the emission of light, and pure hydrogen gas is evolved.

### *Oxides of Potassium.*

Potassium unites with oxygen in two proportions. The protoxide, commonly called *potash* or *potassa*, is always formed when potassium is put into water, or when it is exposed at common temperatures to dry

air or oxygen gas. By the first method the protoxide is obtained in combination with water; in the latter, it is anhydrous. In performing the last mentioned process, the potassium should be cut into very thin slices; for otherwise the oxidation is incomplete. The product, when partially oxidized, was once suspected to be a distinct oxide; but it is now admitted to be a mixture of potassa and potassium.

As potassa is the protoxide of potassium, it is supposed to contain one atom of each of its elements. Its composition is best determined by collecting and measuring the quantity of hydrogen which is evolved when potassium is plunged under water. From the experiments of Sir H. Davy, and Gay-Lussac and Thénard, it appears that 40 grains of potassium decompose precisely 9 grains of water; and that while one grain of hydrogen escapes in the gaseous form, the 8 grains of oxygen combine with the metal. The protoxide of potassium is therefore composed of

Potassium	.	40, or one atom.
Oxygen	.	8, or one atom.

And 48 is its combining proportion.

When potassium burns in the open air or in oxygen gas, it is converted into an orange-coloured substance, which is the peroxide of potassium. It may likewise be formed by conducting oxygen gas over potassa at a red heat. When this peroxide is put into water, it is resolved into oxygen and potassa, the former of which escapes with effervescence, and the latter is dissolved. According to Gay-Lussac and Thénard, it consists of

Potassium	.	40, or one atom.
Oxygen	.	24, or three atoms.

Anhydrous potassa may be prepared either by the slow oxidation of potassium, as already mentioned, or by decomposing nitrate of potassa by a red heat in a vessel of gold. In its pure state, it is a white solid substance, highly caustic, which fuses at a temperature somewhat above that of redness, and bears the strongest heat of a wind furnace without being decomposed or volatilized. It has a powerful affinity for water, and intense heat is disengaged during the act of combination. With a certain portion of that liquid it forms a solid hydrate, the elements of which are united by an affinity so energetic that no degree of heat hitherto employed can effect their separation. This substance was long regarded as the pure alkali, but it is in reality the *hydrate of potassa*. It is composed of 48 parts, or one atom of potassa, and 9 parts, or one atom of water.

The hydrate of potassa is solid at common temperatures. It fuses at a heat rather below redness, and assumes a somewhat crystalline texture in cooling. It is highly deliquescent, and requires about half its weight of water for solution. It is soluble, likewise, in alcohol. It destroys all animal textures, and on this account is employed in surgery as a caustic. It was formerly called *lapis causticus*, but it is now termed *potassa* and *potassa fusa* by the Colleges of Edinburgh and London. This preparation is made by evaporating the aqueous solution of potassa in a silver or clean iron capsule to the consistency of oil, and then pouring it into moulds. In this state it is impure, containing oxide of iron, together with the muriate, carbonate, and sulphate of potassa. It is purified from these substances by dissolving it in alcohol, and evaporating the solution to the same extent as before,



in a silver vessel. The operation should be performed expeditiously, in order to prevent, as far as possible, the absorption of carbonic acid.

The aqueous solution of potassa, the *aqua potassæ* of the Pharmacopœia, is prepared by decomposing the carbonate of potassa by lime. To effect this object completely, it is advisable to employ equal parts of quicklime and carbonate of potassa. After slaking the lime in an iron vessel, the carbonate of potassa, dissolved in its own weight of hot water, is added, and the mixture is boiled briskly for about ten minutes. The liquid, after subsiding, is filtered through a funnel, the throat of which is obstructed by a piece of clean linen.

This process is founded on the fact that lime deprives the carbonate of potassa of its acid, forming an insoluble carbonate of lime, and setting the pure alkali at liberty. If the decomposition is complete, the filtered solution should not effervesce with muriatic acid.

The solution of potassa is highly caustic, and its taste intensely acid. It possesses alkaline properties in an eminent degree, converting the vegetable blue colours to green, and neutralizing the strongest acids. It absorbs carbonic acid gas rapidly, and is consequently employed for withdrawing that substance from gaseous mixtures. For the same reason it should be excluded from the atmosphere during the process of filtering, and preserved in well-closed bottles.

Potassa is employed as a reagent in detecting the presence of bodies, and in separating them from one another. The solid hydrate, owing to its strong affinity for water, is used for depriving gases of hygrometric moisture, and is admirably fitted for forming frigorific mixtures. (Page 42.)

Potassa may be distinguished from all other substances by the following characters. 1. If tartaric acid be added in excess to a salt of potassa dissolved in water, and the solution be stirred with a glass rod, a white precipitate, the bitartrate of potassa, soon appears, which forms peculiar white streaks upon the glass by the pressure of the rod in stirring. 2. A solution of the muriate of platinum causes a yellow precipitate, the muriate of platinum and potassa. This is the most delicate test, provided the mixture be gently evaporated to dryness, and a little cold water be afterwards added. The muriate of platinum and potassa then remains in the form of small shining yellow crystals. 3. By being precipitated by no other substance.

*Chloride of Potassium.*—Potassium takes fire spontaneously in an atmosphere of chlorine, and burns with greater brilliancy than in oxygen gas. This chloride is also generated when potassium is heated in muriatic acid gas, hydrogen being evolved at the same time. It is the residue of the decomposition of the chlorate of potassa by heat; and it is obtained in the form of colourless cubic crystals, when a solution of the muriate of potassa evaporates spontaneously.

The chloride of potassium has a saline and rather bitter taste. It requires three parts of water at 60° F. for solution, and is rather more soluble in hot water. Its solution contains the muriate of potassa. (Page 231.) It is composed of 36 parts or one atom of chlorine, and 40 parts or one atom of potassium.

*Iodide of Potassium.*—This compound is formed, with emission of light, when potassium is heated in contact with iodine. It may likewise be obtained by means of heat from the iodate, and by crystallization from the hydriodate of potassa. It fuses readily when heated, and is volatilized at a temperature below redness. It deliquesces in a moist atmosphere, and is very soluble in water. It dissolves also in

strong alcohol ; and the solution, when gently evaporated, yields small colourless cubic crystals of the iodide of potassium. It is composed of one atom of iodine and one atom of potassium.

*Hydrogen and Potassium.*—These substances unite in two proportions, forming in one case a solid, and in the other a gaseous compound. The latter is produced when the hydrate of potassa is decomposed by iron at a white heat, and it appears also to be generated when potassium burns on the surface of water. It inflames spontaneously in air or oxygen gas ; but on standing for some hours over mercury, the greater part, if not the whole of the potassium, is deposited.

The solid hyduret of potassium was made by Gay-Lussac and Thénard, by heating potassium in hydrogen gas. It is a grey solid substance, which is readily decomposed by heat or contact with water. It does not inflame spontaneously in oxygen gas.

*Sulphuret of potassium.*—Sulphur unites readily with potassium by the aid of heat ; and so much caloric is evolved at the moment of combination, that the mass becomes incandescent. The best method of obtaining a sulphuret in definite proportion is by decomposing the sulphate of potassa according to the process of Berthier or Berzelius. (Page 229.) This sulphuret is composed of one atom of sulphur and one atom of potassium. It has a red colour, fuses below the temperature of ignition, and assumes a crystalline texture in cooling. It is dissolved by water, being converted, with evolution of caloric, into the hydrosulphuret of potassa.

Besides this protosulphuret, Berzelius has described four other compounds, which he obtained by igniting carbonate of potassa with different proportions of sulphur. These are composed of one atom of potassium to 2, 3, 4, and 5 atoms of sulphur.

*Phosphuret of Potassium.*—This compound may be formed by the action of potassium on phosphorus with the aid of a moderate heat. It is converted by water into potassa and phosphuretted hydrogen gas, which inflames at the moment of its formation.

## SECTION II.

### SODIUM.

Sir H. Davy made the discovery of sodium in 1807, a few days after he had discovered potassium. The first portions of it were obtained by means of galvanism ; but it may be procured in much larger quantity by chemical processes, precisely similar to those described in the last section.

Sodium has a strong metallic lustre, and in colour is very analogous to silver. It is so soft at common temperatures, that it may be formed into leaves by the pressure of the fingers. It fuses at 200° F. and rises in vapour at a full red heat. Its specific gravity is 0.972.

Sodium soon tarnishes on exposure to the air, though less rapidly than potassium. When thrown into water it swims upon its surface, occasions violent effervescence and a hissing noise, and is rapidly oxidized ; but no light is visible. The action is stronger with hot

water, and a few scintillations appear; but still there is no flame. In each case, soda is generated, owing to which the water acquires an alkaline re-action, and pure hydrogen gas is disengaged.

*Oxides of Sodium.*—Chemists are acquainted with two definite compounds only of sodium and oxygen. The protoxide or *soda* is a grey white solid, difficult of fusion, which is obtained by burning sodium in dry atmospheric air. It is also formed when sodium is oxidized by water; and its composition may be determined by collecting the hydrogen which is then disengaged. According to the experiments of Sir H. Davy, the results of which differ little from those of Gay-Lussac and Thénard, soda consists of 24 parts of sodium and 8 parts of oxygen. For this reason, 24 is regarded as the atomic weight of sodium, and 32 the combining proportion of soda.

When sodium is strongly heated in an excess of pure oxygen, an orange-coloured substance is formed, which is the peroxide of sodium. It is resolved by water into oxygen and soda; and is composed, according to Gay-Lussac and Thénard, of two atoms of sodium and three atoms of oxygen.

With water soda forms a solid hydrate, easily fusible by heat, which is very caustic, is soluble in water and alcohol, has powerful alkaline properties, and in all its chemical relations is exceedingly analogous to potassa. It is prepared from the solution of pure soda, exactly in the same manner as the corresponding preparations of potassa. The solid hydrate is composed of 32 parts, or one atom of soda, and 9 parts or one atom of water.

Soda is readily distinguished from the other alkaline bases by the following characters. 1. It yields with sulphuric acid a salt, which by its taste and form is easily recognized as glauher salt or sulphate of soda. 2. All its salts are soluble in water, and are not precipitated by any reagent. 3. On exposing its salts by means of platinum wire to the blowpipe flame, they communicate to it a rich yellow colour.

*Chloride of Sodium.*—This compound may be formed directly by burning sodium in chlorine, or by heating it in muriatic acid gas. It is deposited in crystals, when a solution of the muriate of soda is evaporated; for this salt, like the muriate of potassa, exists only while in solution, and is converted into a chloride during the act of crystallizing. Hence sea-water, the chief ingredient of which is muriate of soda, yields chloride of sodium by evaporation; and from this source is derived most of the different kinds of common salt, such as fishery salt, stoved salt, and bay salt, substances essentially the same, and between which the sole difference depends on the mode of preparation. The chloride of sodium is known likewise as a natural product under the name of rock or mineral salt.

The common varieties of salt, of which the rock and bay salt are the purest, always contain small quantities of the sulphate of magnesia and lime, and muriate of magnesia. These earths may be precipitated as carbonates by boiling a solution of salt for a few minutes with a slight excess of carbonate of soda, filtering the liquid, and neutralizing with muriatic acid. On evaporating this solution rapidly, the chloride of sodium crystallizes in hollow four-sided pyramids; but it occurs in regular cubic crystals when the solution is allowed to evaporate spontaneously. These crystals contain no water of crystallization, but decrepitate remarkably when heated, owing to the expansion of water mechanically confined within them.

Pure chloride of sodium has an agreeable saline taste. It fuses at

a red heat, and becomes a transparent brittle mass on cooling. It deliquesces slightly in a moist atmosphere, but undergoes no change when the air is dry. In pure alcohol it is insoluble. It requires twice and a half its weight of water at 60° F. for solution, and its solubility is not increased by heat. Like the soluble chlorides in general, it passes into a muriate while in the act of dissolving. Sulphuric acid decomposes it with evolution of muriatic acid gas, and formation of the sulphate of soda. In composition it is analogous to the chloride of potassium, consisting of one atom of chlorine, and one atom of sodium.

The uses of the chloride of sodium are well known. Besides its employment in seasoning food, and in preserving meat from putrefaction, a property which it possesses in a high degree when pure, it is used for various purposes in the arts, especially for the formation of muriatic acid and the chloride of lime.

The compounds of sodium with iodine, sulphur and phosphorus are so analogous to those which potassium forms with the same elements, that a particular description of them is unnecessary. Sodium does not unite with hydrogen.

## SECTION III.

### LITHIUM.

In the year 1818 M. Arfwedson of Sweden\*, in analyzing the mineral called petalite, discovered the existence of a new alkali, and its presence has since been detected in spodumene, lepidolite, and in several varieties of mica. Berzelius has found it also in the waters of Carlsbad in Bohemia. From the circumstance of its having been first obtained from an earthy mineral, Arfwedson gave it the name of *lithion* (from *λίθος lapideus*), a term since changed in this country to *lithia*. It has hitherto been procured in small quantity only, because spodumene and petalite are rare, and do not contain more than 6 or 8 per cent. of the alkali. It is combined in these two minerals with silica and alumina, whereas potassa is likewise present in lepidolite and lithion-mica, and therefore lithia should be prepared solely from the former.

The best process for preparing lithia is that which was suggested by Berzelius. One part of petalite or spodumene, in fine powder, is mixed intimately with two parts of fluor-spar, and the mixture is heated with three or four times its weight of sulphuric acid, as long as any acid vapours are disengaged. The silica of the mineral unites with fluoric acid, and is dissipated in the form of fluosilicic acid gas, while the alumina and lithia unite with sulphuric acid. After dissolving these salts in water, the solution is boiled with pure ammonia to precipitate the alumina, filtered, evaporated to dryness, and then heated to redness to expel the sulphate of ammonia. The residue is sulphate of lithia.

Sir H. Davy succeeded, by means of galvanism, in obtaining a

\* An. de Ch. et de Ph. vol. x.

white coloured metal like sodium from lithia ; but it was oxidized, and thus reconverted into the alkali, with such rapidity that it could not be collected. Lithia may therefore be regarded as the protoxide of *lithium* ; and, according to the analysis of the sulphate of lithia by Stromeyer and Thomson, lithia is inferred to be composed of

Lithium	.	10 or one atom.
Oxygen	.	8 or one atom.

Consequently, 18 is its combining proportion.

Lithia is distinguished from potassa and soda by its greater neutralizing power, by forming sparingly soluble salts with carbonic and phosphoric acids, and by the circumstance of the chloride of lithium being highly deliquescent, and dissolving freely in strong alcohol. This alcoholic solution burns with a red flame ; and all the salts of lithia, when heated on platinum wire before the blowpipe, tinge the flame of a red colour. Further, when lithia is fused on platinum foil, it attacks that metal, and leaves a dull yellow trace round the spot on which it lay. (Berzelius on the Blowpipe. Children's Translation.

Lithia is distinguished from the alkaline earths by forming soluble salts with sulphuric and oxalic acids ; and by the circumstance that the carbonate of lithia, though sparingly soluble in water, forms with it a solution which gives a brown stain to turmeric paper.

## SECTION IV.

### *BARIUM.*

Sir H. Davy discovered *barium*, the metallic base of baryta, in 1808, by a process suggested by Berzelius and Pontin. It consists in forming carbonate of baryta into a paste with water, and placing a globule of mercury in a little hollow made in its surface. The paste was laid upon a platinum tray which communicated with the positive pole of a galvanic battery of 100 double plates, while the negative wire was brought into contact with the mercury. The baryta was decomposed, and the barium entered into combination with the mercury. This amalgam was then heated in a vessel free of air, by which the mercury was expelled, and the barium obtained in a pure form.

Barium, thus procured, is of a dark gray colour, with a lustre inferior to cast iron. Its density is far greater than water, for it sinks rapidly in strong sulphuric acid. It attracts oxygen with avidity from the air, and in doing so forms a white powder which is baryta. It effervesces strongly from the escape of hydrogen when it is thrown into water, and a solution of baryta is produced. It has hitherto been obtained in very minute quantities, and consequently its properties have not been determined with precision.

*Oxides of Barium.* *Barytes*, or *Baryta*, so called from the great density of its compounds, (from *βαρυς* heavy) was discovered in 1774 by Scheele. It is the sole product of the oxidation of barium in air or water. It may be prepared by decomposing the nitrate of baryta



at a red heat; or, as was ascertained by Dr Hope, by exposing the carbonate of baryta contained in a black lead crucible to an intense white heat; a process which succeeds much better, when the carbonate is intimately mixed with charcoal. Baryta is a gray powder, the density of which is about 4. It requires a very high temperature for fusion. It has a sharp caustic alkaline taste, converts vegetable blue colours to green, and neutralizes the strongest acids. Its alkalinity, therefore, is equally distinct as that of potassa or soda; but it is much less caustic and less soluble in water than those alkalies. In pure alcohol, it is insoluble. It has an exceedingly strong affinity for water. When mixed with that liquid it slakes in the same manner as quicklime, but with the evolution of a more intense heat, which, according to Döbereiner, sometimes amounts to luminousness. The result is a white bulky hydrate, fusible at a red heat, which bears the highest temperature of a smith's forge without parting with its water. It is composed of 73 parts, or one atom of baryta, and 9 parts, or one atom of water.

The hydrate of baryta dissolves in twice its weight of boiling water, and in twenty parts of water at the temperature of 60°. F. (Davy.) A saturated solution of baryta in boiling water deposits on cooling transparent, flattened prismatic crystals, which are composed, according to Mr Dalton, of 78 parts, or one atom of baryta, and 180 parts, or 20 atoms of water.

The aqueous solution of baryta is an excellent test of the presence of carbonic acid in the atmosphere or in other gaseous mixtures. The carbonic acid unites with the baryta, and a white insoluble precipitate, the carbonate of baryta, subsides.

According to the experiments of Dr Thomson, 73 is the combining proportion of baryta; and therefore this earth, assuming it to be the protoxide of barium, is composed of 70 parts or one atom of barium, and one atom of oxygen.

The deutoxide of barium may be formed by conducting dry oxygen gas over pure baryta at a low red heat. This deutoxide, according to Thénard, contains twice as much oxygen as baryta; or is composed of one atom of barium and two atoms of oxygen. This is the substance employed by Thénard in the formation of the deutoxide of hydrogen.

Baryta is distinguished from all other substances by the following characters. 1. By dissolving in water and forming an alkaline solution. 2. By all its soluble salts being precipitated as the white carbonate of baryta by alkaline carbonates, and forming the sulphate of baryta, which is insoluble both in acid and alkaline solutions, by sulphuric acid or any soluble sulphate. 3. By forming with muriatic acid a salt, which crystallizes readily by evaporation in the form of four, six, or eight-sided tables, is insoluble in alcohol, and does not undergo any change on exposure to the air.

The readiest method of forming the salts of baryta is by the action of acids on the native or artificial carbonate.

All the soluble salts of baryta are poisonous. The carbonate of baryta, from being dissolved by the juices of the stomach, likewise acts as a poison. The sulphate, from its perfect insolubility, is inert.

*Chloride of Barium.*—This compound is generated when chlorine gas is conducted over baryta at a red heat, and oxygen gas is disengaged. It may also be formed by heating to redness the crystallized muriate of baryta. It consists of one atom of each of its constituents.

It requires five times its weight of water at 60° F. for solution, and is much more soluble in boiling water.

*Sulphuret of Barium.*—The protosulphuret of barium may be prepared from the sulphate of baryta, (page 229.) It dissolves readily in hot water, forming the hydrosulphuret of baryta. By means of this solution all the chief salts of baryta may be procured. Thus, by adding an alkaline carbonate, the carbonate of baryta is precipitated; and when muriatic acid is added, sulphuretted hydrogen is evolved, and muriate of baryta is produced. A solution of pure baryta may also be obtained from the hydrosulphuret, by boiling it with oxide of copper, until the filtered solution no longer gives a dark precipitate with acetate of lead.

The combinations of barium with the other non-metallic substances have not yet been carefully examined.

## SECTION V.

### STRONTIUM.

The metallic base of strontia, called *strontium*, was discovered by Sir H. Davy by a process analogous to that described in the last section. All that is known respecting its properties is, that it is a heavy metal, similar in appearance to barium, that it decomposes water with evolution of hydrogen, and oxidizes quickly in the air, being converted in both cases into strontia.

From the close resemblance between baryta and strontia, these substances were once supposed to be identical. Dr Crawford, however, and M. Sulzer noticed a difference between them; but the existence of strontia was first established with certainty in the year 1792 by Dr Hope\*, and the same discovery was made about the same time by Klaproth†. It was originally extracted from strontianite, the native carbonate of strontia, a mineral found at Strontian in Scotland; and hence the origin of the term *Strontites* or *Strontia*, by which the earth itself is designated.

Pure strontia may be prepared from the nitrate and carbonate of strontia, in the same manner as baryta. It resembles this earth in appearance, in infusibility, and in possessing distinct alkaline properties. It slakes when mixed with water, causing an intense heat, and forming a white solid hydrate, which consists of 52 parts or one atom of strontia, and 9 parts or one atom of water. The hydrate of strontia fuses readily at a red heat, but sustains the strongest heat of a wind furnace without decomposition. It is insoluble in alcohol. Boiling water dissolves it freely, and a hot saturated solution, on cooling, deposits transparent crystals in the form of thin quadrangular tables. These crystals are composed, according to the analysis of Dr Hope, of 52 parts or one atom of strontia and 108 parts or one atom of water. They are converted by heat into the proto-hydrate. They require 50

\* Edinburgh Philosophical Transactions, vol. iv.

† Klaproth's Contributions, vol. i.

times their weight of water at 60° F. for solution, and twice their weight at 212° F. (Dalton.)

The solution of strontia has a caustic taste and alkaline reaction. Like the solution of baryta it is a delicate test of the presence of carbonic acid in air or other gaseous mixtures, forming with it the insoluble carbonate of strontia.

The atomic weight of strontia, as deduced from the analyses of Berzelius, Stromeyer, and Thomson, is 52; and consequently strontia, regarded as the protoxide of strontium, is composed of

Strontium	:	:	44 or one atom.
Oxygen	:	:	8 or one atom.

The deutoxide of strontium is prepared in the same manner as the corresponding preparation of baryta. It may likewise be formed by pouring an aqueous solution of strontia into the deutoxide of hydrogen. According to Thénard, it contains twice as much oxygen as the protoxide.

The soluble salts of strontia, like those of baryta, are precipitated by alkaline carbonates, and by sulphuric acid or soluble sulphates. Strontia is distinguished from baryta by forming with muriatic acid a salt, which crystallizes in the form of slender hexagonal prisms, deliquesces in a moist atmosphere, and dissolves freely in pure alcohol. The alcoholic solution, when set on fire, burns with a blood-red flame; and the salts of strontia, when exposed to the blow-pipe flame on platinum wire, impart to it a red tinge.

The salts of strontia are most conveniently prepared from the carbonate. These compounds are not poisonous.

The chloride of strontium is formed under precisely the same circumstances as the chloride of barium, and its composition is analogous. It is exceedingly soluble in boiling water, and requires twice its weight of water at 60° F. for solution. As already mentioned, it is soluble in alcohol.

The sulphuret of strontium may be prepared by the processes referred to in the last section. It may be advantageously employed for forming the solution and salts of strontia, in the same manner as those of baryta are prepared from the sulphuret of barium.

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## SECTION VI.

### CALCIUM.

The existence of calcium, the metallic base of lime, was demonstrated by Sir H. Davy by a process similar to that described in the section on barium. It is of a whiter colour than barium or calcium, and is converted into lime by being oxidized. Its other properties are unknown.

When carbonate of lime is exposed to a white or even to a very strong red heat, carbonic acid is expelled, and pure lime, commonly called *quicklime*, remains. If lime of great purity is required, it should be prepared from pure carbonate of lime, such as Iceland-spar or Carrara marble; but in burning lime in lime-kilns for making mor-

tar, common lime-stone is employed. The expulsion of carbonic acid is facilitated by mixing the carbonate with combustible substances, in which case carbonic oxide is generated. (Pages 148-49.)

Lime is a brittle white earthy solid, the specific gravity of which is about 2.3. It phosphoresces powerfully when heated to full redness, a property which it possesses in common with strontia and baryta. It is one of the most infusible bodies known; fusing with difficulty, even by the heat of the oxy-hydrogen blowpipe. It has a powerful affinity for water, and the combination is attended with great increase of temperature, and formation of a white bulky hydrate, which is composed of 28 parts or one atom of lime, and 9 parts or one atom of water. The process of *slaking* lime consists in forming this hydrate, and the hydrate itself is called *slaked* lime. It differs from the hydrates of strontia and baryta in parting with its water at a red heat.

The hydrate of lime is dissolved very sparingly by water, and it is a singular fact, first noticed I believe by Mr Dalton, that it is more soluble in cold than in hot water. Thus he found that one grain of lime requires for solution

778 grains of water	.	at 60° F.
972	."	130°
1270	."	212°

And consequently, on heating a solution of lime, or *lime-water*, which has been prepared in the cold, a deposition of lime ensues. This fact was determined experimentally by Mr Phillips, who has likewise observed that water at 32° F. is capable of dissolving twice as much lime as at 212° F.

Owing to this circumstance pure lime cannot be made to crystallize in the same manner as baryta or strontia. Gay-Lussac succeeded, however, in obtaining crystals of lime by evaporating lime water under the exhausted receiver of an air-pump by means of sulphuric acid, (page 49.) Small transparent crystals, in the form of regular hexaedrons are deposited, which consist of water and lime in the same proportion as the hydrate above mentioned.

Lime water is prepared by mixing the hydrate of lime with water, agitating the mixture repeatedly, and then setting it aside in a well-stopped bottle until the undissolved parts shall have subsided. The substance called *milk* or *cream* of lime is made by mixing the hydrate of lime with a sufficient quantity of water to give it the liquid form;—it is merely lime water in which hydrate of lime is mechanically suspended.

Lime water has a harsh acid taste, and converts vegetable blue colours to green.—It agrees, therefore, with baryta and strontia in possessing distinct alkaline properties. Like the solutions of these earths, it has a strong affinity for carbonic acid, and forms with it an insoluble carbonate. On this account lime water should be carefully protected from the air. For the same reason, lime water is rendered turbid by a solution of carbonic acid; but on adding a large quantity of the acid, the transparency of the solution is completely restored, because carbonate of lime is soluble in an excess of carbonic acid. The action of this acid on the solutions of baryta and strontia is precisely similar.

The atomic weight of lime, as deduced from the experiments of Dr Thomson, is 28; and therefore lime, regarded as the protoxide of calcium, is composed of 20 parts or one atom of calcium, and one atom of oxygen.

The deutoxide of calcium may be formed in the same way as the deutoxide of strontium. According to Thénard it consists of one atom of calcium and two atoms of oxygen.

The salts of lime, which are easily prepared by the action of acids on pure marble, are in many respects similarly affected by reagents, as those of baryta and strontia. They are precipitated, for example, by alkaline carbonates. Sulphuric acid and soluble sulphates likewise precipitate lime from a moderately strong solution. But the sulphate of lime has a considerable degree of solubility. Thus, a dilute solution of a salt of lime is not precipitated at all by sulphuric acid; and when the sulphate of lime is separated, it may be redissolved by the addition of nitric acid.

The most delicate test of the presence of lime is oxalate of ammonia; for of all the salts of lime, the oxalate is the most insoluble in water. This serves to distinguish lime from most substances, though not from baryta and strontia; because the oxalates of baryta and strontia, especially the latter, are likewise sparingly soluble.—All these oxalates dissolve readily in water acidulated with the nitric or muriatic acid.

The best characters for distinguishing lime from the two other alkaline earths are the following. The nitrate of lime yields prismatic crystals by evaporation, is deliquescent in a high degree, and is very soluble in alcohol. The nitrates of baryta and strontia crystallize in regular octahedrons or segments of an octahedron, undergo no change on exposure to the air, and do not dissolve in pure alcohol.

The salts of lime, when heated before the blowpipe, or when their solutions in alcohol are set on fire, communicate to the flame a dull brownish-red colour.

*Chloride of Calcium.*—The chloride of calcium is formed in the same manner as the chloride of strontium. In decomposing the muriate of lime by heat, a little muriatic acid is sometimes expelled as well as water. The chloride of calcium is soluble in alcohol, and deliquesces rapidly on exposure to the atmosphere. On account of its strong affinity for water, it is much employed to deprive gases and other substances of their moisture. For a like reason, it may be used for forming frigorific mixtures with snow; but for this purpose the crystallized muriate of lime, which contains six atoms of water of crystallization, is far preferable.

The chloride of calcium contains one atom of each of its elements.

*Chloride of Lime.*—This compound, commonly called *oxymuriate of lime* or *bleaching powder*, is prepared by exposing thin strata of recently slaked lime in fine powder to an atmosphere of chlorine. The gas is absorbed in large quantity, and combines directly with the lime.

The chloride of lime is a dry white powder, which smells faintly of chlorine, and has a strong taste. It dissolves partially in water, and the solution possesses powerful bleaching properties, and contains both chlorine and lime; while the undissolved portion is hydrate of lime, retaining a small quantity of chlorine. The aqueous solution, when exposed to the atmosphere, is gradually decomposed;—chlorine is set free, and carbonate of lime is generated. On boiling the liquid, muriatic, and I presume chloric, acid are formed; and by long keeping, the dry chloride appears to undergo a similar change, at least muriatic acid is produced in large quantity. The chloride of lime is also decomposed by a strong heat. At first, chlorine is evolved; but pure



oxygen is afterwards disengaged, and chloride of calcium remains in the retort.

The composition of the chloride of lime was first carefully investigated by Mr Dalton\*, and it has since been analyzed by Dr Thomson†, M. Welter‡, and Dr Ure§. The three first mentioned chemists infer from their researches that the bleaching powder is a hydrated *sub-chloride* or *di-chloride* of lime, in which 36 parts or one atom of chlorine are united with 56 parts or two atoms of lime. They are also of opinion that, on mixing this sub-chloride with water, a real chloride is dissolved, and one atom of lime is separated. Dr Ure, on the contrary, denies that the bleaching powder is a sub-chloride; and maintains, according to the result of his own analysis, that the elements of this compound do not constitute a regular atomic combination.

Several methods have been proposed for estimating the value of different specimens of the chloride of lime. Perhaps the most convenient for the artist is that of Welter, which consists in ascertaining the power of the bleaching liquid to deprive a solution of indigo of known strength of its colour. For analytical purposes, the best method is to decompose the chloride of lime, confined in a glass tube over mercury, by means of muriatic acid. The muriate of lime is generated, and the chlorine being set free, its quantity may easily be measured.

The *protosulphuret of calcium* is procured by processes similar to those for forming the sulphuret of barium.

The phosphorescent substance called *Canton's phosphorus*, which is made by exposing a mixture of calcined oyster shells and sulphur to a red heat, is supposed to be a sulphuret of lime; but its real composition has not been determined.

*Phosphuret of Lime*.—This compound is formed by passing the vapour of phosphorus over fragments of quicklime at a red heat. The true nature of the product is not known with certainty. It is either a phosphuret of lime, or a mixture of phosphuret of lime and phosphuret of calcium. When it is put into water, mutual decomposition ensues, and phosphuretted hydrogen, hypophosphorous acid, and phosphoric acid are generated.

## SECTION VII.

### MAGNESIUM.

The galvanic researches of Sir H. Davy have demonstrated the existence of magnesium, though he obtained it in a quantity too minute for determining its properties. He ascertained, however, that it decomposes water, and is converted by mixing with oxygen into magnesia.

Magnesia, the only known oxide of magnesium, is obtained by exposing the carbonate of magnesia to a very strong red heat, by which the carbonic acid is expelled. It is a white insoluble powder, of an earthy appearance; when pure, it has neither taste nor odour. Its specific gra-

\* Annals of Philosophy, vol. i. and ii.

† Ibid. vol. xv.

‡ An. de Ch. et de Ph. vol. viii.

§ Quarterly Journal, vol. xiii.

vity is about 2.3. It is exceedingly infusible. It has a weaker affinity than lime for water; for, though it forms a hydrate when moistened, the combination is effected with hardly any disengagement of caloric, and the product is readily decomposed by a red heat. There probably exist several different compounds of water and magnesia, but the native hydrate is the only one known with certainty. According to the analysis of Stromeyer, this hydrate contains one atom of each of its constituents; and the results of the analyses of Berzelius and Dr Fyfe accord very nearly with this proportion.

Magnesia dissolves very sparingly in water. According to Dr Fyfe, it requires 5142 times its weight of water at 60°, and 36,000 of boiling water for solution. The resulting liquid does not change the colour of violets; but when pure magnesia is put upon moistened turmeric paper, it causes a brown stain. From this there is no doubt that the interaction of magnesia with respect to vegetable colours, when tried in the ordinary mode, is owing to its insolubility.—It possesses the still more essential character of alkalinity, that, namely, of forming neutral salts with acids, in an eminent degree. It absorbs both water and carbonic acid when exposed to the atmosphere, and therefore should be kept in well-closed phials.

The atomic weight of magnesia, as determined by Dr Thomson, is 20. Consequently this alkaline base, regarded as the protoxide of magnesium, is composed of

Magnesium	12 or one atom,
Oxygen	8 or one atom.

Magnesia is characterized by the following properties. With the nitric and muriatic acids it forms salts which are soluble in alcohol, and exceedingly deliquescent. The sulphate of magnesia is very soluble in water, a circumstance by which it is distinguished from the alkaline earths. Magnesia is precipitated from its salts as a bulky hydrate by the pure alkalies. It is precipitated as carbonate of magnesia, by the carbonates of potassa and soda; but the bicarbonates, and the common carbonate of ammonia, do not precipitate it in the cold. If moderately diluted, the salts of magnesia are not precipitated by oxalate of ammonia. By means of this reagent magnesia may be both distinguished and separated from lime.

The compounds of magnesium with the other simple substances have little interest. The chloride is formed by decomposing the muriate of magnesia by heat; but it is apt to lose a portion of muriatic acid during the process. It is very deliquescent, and is soluble in alcohol. It is composed of one atom of chlorine and one atom of magnesium.

## SECTION VIII.

### *ALUMINUM.*

That alumina is an oxidized body is certain, for Sir H. Davy ascertained that potassa is generated when the vapour of potassium is brought into contact with pure alumina heated to whiteness. It is

likewise probable, from the experiments of the same philosopher, that the base of this earth, though not yet obtained in a separate state, is of a metallic nature. To this supposed metal the term *aluminum* is applied.

Alumina is one of the most abundant productions of nature. It is found in every region of the globe, and in rocks of all ages, being a constituent of the oldest primary mountains, of the secondary strata, and of the most recent alluvial depositions. The different kinds of clay of which bricks, pipes, and earthen-ware are made, consist of the hydrate of alumina in a greater or less degree of purity. Though this earth commonly appears in rude amorphous masses, it is sometimes found beautifully crystallized.—The ruby and the sapphire, two of the most beautiful gems with which we are acquainted, are composed almost solely of alumina.

Pure alumina is procured for chemical purposes from common alum, the sulphate of alumina and potassa. When this salt is digested with excess of ammonia or of the fixed alkaline carbonates, the alumina is precipitated in the form of a white bulky hydrate. This precipitate, when carefully washed and heated to whiteness, yields pure anhydrous alumina. An easier process, proposed by Gay-Lussac, is to expose the sulphate of alumina and ammonia to a strong heat, so as to expel the ammonia and sulphuric acid.

Alumina has neither taste nor smell, and is quite insoluble in water. It is very infusible, though less so than lime or magnesia. It has a powerful affinity for water, attracting moisture from the atmosphere with avidity; and for a like reason, it adheres tenaciously to the tongue when applied to it. Mixed with a due proportion of water, it yields a soft cohesive mass, susceptible of being moulded into regular forms, a property upon which depends its employment in the art of pottery. When once moistened, it cannot be rendered anhydrous, except by exposure to a full white heat; and in proportion as it parts with water, its volume diminishes. (33.)

Alumina most probably forms several different hydrates with water. Dr Thomson has described two definite compounds of this kind. One is the bi-hydrate, composed of one atom of alumina to two atoms of water; and it is procured by exposing, for the space of two months, alumina, precipitated by means of an alkali, to a dry air, the temperature of which does not exceed 60° F. The other compound is a protohydrate, obtained by drying the bi-hydrate at a temperature of 100° F., by which means half of its water is expelled.

Alumina, owing to its insolubility, does not affect the blue colour of plants. The earth appears to possess the properties both of an acid and of an alkali;—of an acid, by uniting with alkaline bases, such as potassa, lime, and baryta;—of an alkali, by forming salts with acids. In neither case, however, are its soluble compounds neutral.

Dr Thomson, after a most elaborate investigation, fixes upon 18 as the atomic weight of alumina. (First Principles, vol. i.) If, therefore, alumina is regarded as the protoxide of aluminum, it is composed of

Aluminum	.	.	10 or one atom.
Oxygen	.	.	8 or one atom.

Alumina is easily recognised by the following characters. 1. It is separated from acids, as a hydrate, by all the alkaline carbonates, and

by pure ammonia. 2. It is precipitated by pure potassa or soda, but the precipitate is completely re-dissolved by an excess of the alkali.

The compounds of aluminum with the other simple non-metallic bodies have not yet been investigated.

## SECTION IX.

### GLUCINUM, YTTRIUM, ZIRCONIUM.

#### *Glucinum.*

*Glucina*, which was discovered by Vauquelin in 1798, has hitherto been found only in three rare minerals, the euclase, beryl, and emerald. It is supposed by analogy to be the oxide of a metal, and its supposed metallic base is called *Glucinum*.

Glucina is a white powder, which has neither taste nor odour, and is quite insoluble in water. Its specific gravity is 3. Vegetable colours are not affected by it. The salts which it forms with acids have a sweetish taste, a circumstance which distinguishes glucina from other earths, and from which its name is derived\*. According to the analysis of Dr Thomson and Berzelius, 26 is the atomic weight of glucina.

Glucina may be known chemically by the following characters. 1. Pure potassa or soda precipitates glucina from its salts, but an excess of the alkali redissolves it. 2. It is precipitated permanently by pure ammonia as the hydrate, and by fixed alkaline carbonates, as the carbonate of glucina. 3. It is dissolved completely by a cold solution of carbonate of ammonia, and is precipitated from it by boiling. By means of this property, glucina may be both distinguished and separated from alumina.

#### *Yttrium.*

*Yttrium* is the supposed metallic base of an earth which was discovered in 1794, by Professor Gadolin, in a mineral found at Ytterby in Sweden, from which it received the name of Yttria.

Yttria resembles alumina and glucina in its chemical properties; but is distinguished from both by being insoluble in a solution of pure potassa. Its atomic weight, as deduced by Dr Thomson from the analyses of Berzelius, is 42.

The substance called *thorina*, supposed by Berzelius to be a distinct earth, has recently been recognised by that chemist as the phosphate of yttria.

#### *Zirconium.*

The experiments of Sir H. Davy proved zirconia to be an oxidized

\* From *γλυκὺς* sweet.

body, and afforded a presumption that its base, *zirconium*, is of a metallic nature. The decomposition of this earth, however, had not been effected in a satisfactory manner till the year 1824, when Berzelius succeeded in obtaining zirconium in an insulated state.

Zirconium is procured by heating a mixture of potassium with the fluato of zirconia and potassa, carefully dried, in a tube of glass or iron, by means of a spirit-lamp. The reduction takes place at a temperature below redness, and without emission of light. The mass is then washed with boiling water, and afterwards digested for some time in dilute muriatic acid. The residue is pure zirconium.

Zirconium, thus obtained, is in the form of a black powder, which may be boiled in water without being oxidized, and is attacked with difficulty by the sulphuric, muriatic, or nitro-muriatic acids; but is dissolved readily and with disengagement of hydrogen by fluoric acid. Heated in the open air it takes fire at a temperature far below luminousness, burns brightly, and is converted into zirconia. Its metallic nature seems somewhat questionable. It may indeed be pressed out into thin shining scales of a dark grey colour, and of a lustre which may be called metallic; but its particles cohere together very feebly, and it is not a conductor of electricity. These points, however, require further investigation before a decisive opinion on the subject can be adopted\*.

Zirconia was discovered in 1789 by Klaproth in the Jargon or Zircon of Ceylon, and has since been found in the Hyacinth from Expailly in France. It is an earthy substance, resembling alumina in appearance, of specific gravity 4.3, having neither taste nor odour, and quite insoluble in water. Its colour, when pure, is white; but it has frequently a tinge of yellow, owing to the presence of iron, from which it is separated with great difficulty. Its salts are distinguished from those of alumina or glucina by being precipitated by all the pure alkalies, in an excess of which it is insoluble. The alkaline carbonates precipitate it as the carbonate of zirconia, and a small portion of it is redissolved by an excess of the precipitant.

The composition of zirconia has not yet been satisfactorily determined. From some analyses by Berzelius, described in the essay above referred to, it is probable that the atomic weight of this earth is about 30 or 33.

## SECTION X.

### *SILICIUM.*

That silica or siliceous earth is composed of a combustible body united with oxygen, was demonstrated by Sir H. Davy; for on bringing the vapour of potassium in contact with pure silica heated to whiteness, a compound of silica and potassa resulted, through which was diffused the inflammable base of silica in the form of black parti-

\* Poggendorff's *Annalen*, vol. iv. or *Quarterly Journal of Science*, vol. xvii.



cles like plumbago. To this substance, on the supposition of its being a metal, the term *silicium* was applied. But though this view has been adopted by most chemists, so little was known with certainty concerning the real nature of the base of silica, that Dr Thomson inclined to the opinion of its being a non-metallic body, and accordingly associated it in his system of chemistry with carbon and boron under the name of *silicon*. The recent researches of Berzelius appear decisive of this question. A substance which wants the metallic lustre, and is a non-conductor of electricity, cannot be regarded as a metal. It may not be improper, however, to have this subject more fully investigated, before separating silica from a class of bodies with which, in several respects, it is so nearly allied.

Pure silicium was procured by Berzelius in the year 1824, by the action of potassium on fluosilicic acid gas. The most convenient method of preparing it is by heating potassium with the dry fluuate of silica and potassa. The residue, after being well washed with hot water, is heated to redness to expel a little hydrogen which was united to the silicium, and it is then digested in dilute fluoric acid, with the view of dissolving adherent particles of silica.

Silicium obtained in this manner has a dark nut-brown colour, without the least trace of metallic lustre. It is a non-conductor of electricity. It is incombustible in air and in oxygen gas; and may be exposed to the flame of the blow-pipe without fusing or undergoing any other change. It is neither dissolved nor oxidized by the sulphuric, nitric, muriatic, or fluoric acids; but a mixture of the nitric and fluoric acids dissolves it readily even in the cold.

Silicium is not changed by ignition with chlorate of potassa. In nitre it does not deflagrate until the temperature is raised so high that the acid is decomposed; and then the oxidation is effected by the affinity of the disengaged alkali for silica co-operating with the attraction of oxygen for silicium. For a similar reason it burns vividly when brought into contact with the carbonate of potassa or soda, and the combustion ensues at a temperature considerably below redness. It explodes, in consequence of a copious evolution of hydrogen, when it is dropped upon the fused hydrates of potassa, soda, or baryta.

### *Oxide of Silicium or Silica.*

Silica exists in the earth in great quantity. It enters into the composition of most of the earthy minerals; and under the name of quartz rock, forms independent mountainous masses. It is the chief ingredient in sand-stones; and flint, calcedony, rock crystal, and other analogous substances, consist almost solely of silica. Siliceous earth of sufficient purity for most purposes may, indeed, be procured by igniting transparent specimens of rock crystal, throwing them while red-hot into water, and then reducing them to powder.

Pure silica, in this state, is a light white powder, which feels rough and dry when rubbed between the fingers, and is both insipid and inodorous. It is fixed in the fire, and is very infusible; but fuses before the oxy-hydrogen blow-pipe with greater facility than lime or magnesia.

In its solid form it is quite insoluble in water; but Berzelius has shown that, when silica in the nascent state is in contact with that fluid, it is dissolved in large quantity. On evaporating the solution gently, a bulky gelatinous substance separates, which is the hydrate

of silica. This hydrate is partially decomposed by a very moderate temperature ; but a red heat is required for expelling the whole of the water. According to Dr Thomson, silica unites with water in several proportions. (First Principles, vol. i. p. 191.)

Silica, most likely from its insolubility, does not change the blue vegetable colours. It appears to possess the properties of an acid rather than of an alkali. Thus, no acid acts upon silica except the fluoric acid ; whereas it is dissolved by solutions of the fixed alkalies, and combines with many of the metallic oxides. On this account silica is termed *silicic acid* by some chemists, and its compounds with alkaline bases *silicates*. The compound earthy minerals that contain silica may be regarded as native silicates.

The combination of silica with the fixed alkalies is best effected by mixing pure sand with the carbonate of potassa or soda, and heating the mixture to redness. During the process, carbonic acid is expelled, and a silicate of the alkali is generated. The nature of the product depends upon the proportions which are employed. On igniting one part of silica with three of the carbonate of potassa, a vitreous mass is formed, which is deliquescent, and may be dissolved completely in water. This solution, which was formerly called *liquor silicum*, has an alkaline reaction, and absorbs carbonic acid on exposure to the atmosphere, by which it is partially decomposed. Concentrated acids precipitate the silica as a gelatinous hydrate ; but if a considerable quantity of water is present, and the acid is added gradually, the alkali may be perfectly neutralized without any separation of silica. When a solution of this kind is evaporated to dryness, the silica is rendered quite insoluble, and may thus be obtained in a pure form.

But if the proportion of silica and alkali is reversed, a transparent brittle compound results, which is insoluble in water, is attacked by none of the acids excepting the fluoric, and possesses the well-known properties of glass. Every kind of glass is composed of silica and an alkali, and all its varieties are owing either to differences in the proportion of the constituents, to the nature of the alkali, or to the presence of foreign matters. Thus the green bottle glass is made of impure materials, such as river sand, which contains iron, and the most common kind of kelp or pearl ashes. Crown glass for windows is made of a purer alkali, and sand which is free from iron. Plate glass, for looking glasses, is composed of sand and alkali in their purest state ; and in the formation of flint glass, besides these pure ingredients, a considerable quantity of litharge or red lead is employed. A small portion of the peroxide of manganese is also used, in order to oxidize carbonaceous matters contained in the materials of the glass ; and nitre is sometimes added with the same intention.

Berzelius ascertained the composition of silica by oxidizing a known quantity of silicium, and weighing the product carefully ; and according to this synthetic experiment, 100 parts of silica are composed of 48 parts of silicium and 52 parts of oxygen. The atomic weight of silica, deduced apparently with great care by Dr Thomson, is precisely 16. Admitting, therefore, that an atom of silica contains 8 parts or one atom of oxygen, (and it manifestly, if 16 is its equivalent, cannot contain more than one atom,) it follows that the remaining 8 parts must be silicium, an inference which accords very nearly with the experimental result of Berzelius. Consequently, 8 must be the atomic weight of silicium, and silica is its protoxide.

*Fluosilicic Acid Gas.*

This gas is formed whenever fluoric acid comes in contact with siliceous earth; and this is the reason why pure fluoric acid can be prepared in metallic vessels only, and with fluor spar that is free from rock crystal. The most convenient method of procuring the gas is to mix in a retort one part of pulverized fluor spar with its own weight of sand or pounded glass, and two parts of strong sulphuric acid. On applying a gentle heat, fluosilicic acid gas is disengaged with effervescence, and may be collected over mercury.

This compound is a colourless gas, which extinguishes flame, destroys animals that are immersed in it, and irritates the respiratory organs powerfully. It does not corrode glass vessels provided they are quite dry. When mixed with atmospheric air it forms a white cloud, owing to the presence of watery vapour. Its specific gravity, according to Dr Thomson, is 3.6111; and 100 cubic inches of it, at 60° F. and when the barometer stands at 30 inches, weigh 110.138 grains.

Water acts powerfully on fluosilicic acid gas, of which it condenses, according to Dr John Davy, 263 times its volume. (Philos. Trans. for 1812.) The gas suffers decomposition at the moment of contact with water, depositing a part of its silica in the form of gelatinous hydrate. The liquid, which has a sour taste and reddens litmus paper, contains the whole of the fluoric acid, together with two thirds of the silica which was originally present in the gas. (Berzelius.) By conducting fluoric acid gas into a solution of ammonia, complete decomposition ensues;—fluosilicic acid unites with the alkali, forming fluate of ammonia, and all the silica is deposited. On this fact is founded the mode of analyzing fluosilicic acid adopted by Dr Davy and Dr Thomson. According to Dr Thomson, whose result may be regarded as nearer the truth than that of Dr Davy, this gas is composed of

Fluoric acid	.	.	10 or one atom.
Silica	.	.	16 or one atom.

and 26 is its combining proportion.

The prevailing opinion respecting the nature of this compound is that it is an acid capable of combining with alkalis; and its salts are termed *fluosilicates*. The foundation of this opinion rests upon the facts that it reddens litmus paper, and combines with twice its volume of ammoniacal gas, forming a dry white salt. Berzelius has recently adopted a different view. He maintains that it is not an acid, but a real gaseous salt, the fluate of silica, of which fluoric acid is the acid and silica the base. He regards the fluosilicates as double salts, which are composed of the fluate of an alkali united with the fluate of silica. (An de Ch. et de Ph. vol. xxvii.)

## SECTION XI.

*MANGANESE.*

Manganese, which was discovered in 1774 by Gahn and Scheele, is a hard brittle metal, of a grayish-white colour, and granular texture. Its specific gravity is 6.85. When pure it is not attracted by the mag-

net. It is exceedingly infusible, requiring a heat of  $160^{\circ}$  Wedgwood for fusion. It soon tarnishes on exposure to the air, and absorbs oxygen with rapidity when heated to redness in open vessels. Pure water does not act upon it at common temperatures; but if watery vapour be passed over manganese at a red heat, oxidation of the metal ensues, and hydrogen gas is disengaged. The decomposition of water is likewise occasioned by dilute muriatic or sulphuric acid, and the muriate or sulphate of the protoxide of manganese is the product.

Manganese, owing doubtless to its powerful affinity for oxygen, has never been found in an uncombined state in the earth; but the peroxide of manganese occurs abundantly. This metal retains its oxygen with such force that its oxides require a stronger heat for reduction than potassa or soda. The method by which Gahn succeeded in procuring metallic manganese, was by exposing the peroxide, surrounded with charcoal, to the most intense heat of a smith's forge; and this process has been successfully repeated by others. (Berthier in *An. de Ch. et de Ph.* vol. xx.)

### *Oxides of Manganese.*

Different opinions have prevailed concerning the number of the oxides of manganese; nor do chemists, even at present, seem quite decided upon the subject. It is certain, however, that there are three distinct oxides; and it appears from the experiments of Thomson\*, whose results agree closely with those of Aifwedson†, and Berthier‡, that they are thus constituted:—

	<i>Manganese.</i>	<i>Oxygen.</i>
Protoxide .	28, or one atom.	8, or one atom.
Deutoxide .	28 . .	12, or $1\frac{1}{2}$ atom.
Peroxide .	28 . .	16, or 2 atoms.

*Peroxide.* This is the well-known ore commonly called from its colour the black oxide of manganese, the nature of which was ascertained in 1774 by Scheele. It generally occurs massive, of an earthy appearance, and mixed with other substances, such as siliceous and aluminous earths, oxide of iron, and carbonate of lime. It is sometimes found, on the contrary, in the form of prismatic crystals, of a brownish-black colour, and imperfect metallic lustre. I possess a crystallized specimen of this kind from Ilfeld in the Harz, which is quite pure. This oxide may be made artificially by exposing the nitrate of manganese to a commencing red heat, until the whole of the nitric acid is expelled.

The peroxide of manganese undergoes no change on exposure to the air. It is insoluble in water, and does not unite either with acids or alkalies. When boiled with sulphuric acid, it yields oxygen gas, and a sulphate of the protoxide is formed. (Page 110.) With muriatic acid, a muriate of the protoxide is generated, and chlorine is evolved. (Page 163.) On exposure to a red heat, it is converted, with evolution of oxygen gas, into the deutoxide of manganese. (Page 110.)

The peroxide of manganese is employed in the arts, in the manu-

\* First Principles, vol. i.

† Letter from Berzelius in the *Annales de Ch. et de Ph.* vol. vi.

‡ Ibid. xx.

facture of glass, and in preparing chlorine for bleaching. In the laboratory it is used for procuring chlorine and oxygen gases, and in the preparation of the salts of manganese.

*Deutoxide.* This oxide combined with water sometimes occurs native. It is readily procured by exposing the peroxide of manganese to a low red heat; and it is, therefore, the chief residue of the usual process for forming oxygen. By exposure to a white heat it is converted into what is called the red oxide of manganese.

The deutoxide, when reduced to powder, is of a brown colour. On exposure to the air, it slowly absorbs oxygen, and passes into the state of peroxide. It is dissolved by strong sulphuric and muriatic acids in the cold, forming deep red-coloured solutions. With strong nitric acid it yields a soluble protonitrate, and an insoluble black powder, which is the peroxide. (Berthier.)

*Protoxide.* The protoxide is formed when a mixture of the deutoxide of manganese and charcoal is exposed to a strong red heat; or by passing a current of hydrogen gas over the deutoxide heated to redness in a tube of porcelain. This oxide is of a green colour when pure, but becomes brown on exposure to the air, owing to the absorption of oxygen. It is contained in all the salts of manganese, and, indeed, it is the only oxide of this metal which is capable of forming regular salts with acids.

The sulphate and muriate of manganese are formed when the peroxide of manganese is heated with sulphuric or muriatic acid. Prepared in this way, however, they always contain iron and other impurities. A convenient method of forming a pure muriate is by heating to redness a mixture of the peroxide of manganese with an equal weight of the muriate of ammonia. In this process the chlorine of the muriatic acid unites with the metal of the oxide to the exclusion of every other substance, provided an excess of manganese be present. The resulting chloride is then dissolved in water, and the insoluble matters separated by filtration. (Faraday in Quarterly Journal, vol. vi.)

The salts of manganese are either colourless, or have a pink hue. The protoxide is precipitated from their solutions, as the white hydrate by ammonia, or the pure fixed alkalies; as the white carbonate of manganese by alkaline carbonates and bicarbonates; as the white ferrocyanate of manganese, by the ferrocyanate of potassa, a character by which the absence of iron may be demonstrated. These white precipitates, with the exception of that obtained by means of a bicarbonate, very soon become brown from the absorption of oxygen. None of the salts of manganese which contain a strong acid, such as the nitric, muriatic, or sulphuric acid, are precipitated by sulphuretted hydrogen. With an alkaline hydrosulphuret, on the contrary, a flesh-coloured precipitate is formed, which is either a hydrosulphuret of the protoxide, or a hydrated protosulphuret of metallic manganese. When heated in close vessels, it yields a dark coloured sulphuret, and water is evolved.

The substance called the *red oxide* of manganese is formed by exposing the peroxide or deutoxide to a white heat, either in close or open vessels. It has a brownish-red colour when in powder. Fused with borax or glass, it communicates to it a beautiful violet hue; and it is the cause of the colour of the amethyst. Concentrated hot nitric acid acts upon it in the same manner as on the deutoxide.

The red oxide contains more oxygen than the protoxide, and less than the deutoxide. According to Arfwedson, it consists of 28 parts



of manganese, and 10.4 parts of oxygen, quantities which do not correspond with the laws of combination. Its title to be ranked as a distinct oxide of manganese may, therefore, be questioned; and I have reason to suspect, from a series of experiments on this subject, as yet however incomplete, that the composition of this oxide varies with the degree of heat to which it has been exposed. It is probably a mixture or compound of the protoxide and deutoxide.

It has been inferred from some experiments of Berzelius and John, that there are two other oxides of manganese, which contain less oxygen than the green or protoxide. We have no proof, however, of the existence of such compounds.

Besides the oxides of manganese which have been described, this metal is capable of forming two acids with oxygen, the *manganeseous* and the *manganesic acid*. The history of these compounds is the following. When the peroxide of manganese is mixed with an equal weight of nitre or carbonate of potassa, and the mixture is exposed to a red heat, a green-coloured fused mass is formed, which has been long known under the name of *mineral chameleon*. On putting this substance into water, a green solution is obtained, the colour of which soon passes into blue, purple, and red; and ultimately a brown flocculent matter, the deutoxide of manganese, subsides, and the liquid becomes colourless. These changes take place more rapidly by dilution, or by employing hot water.

We are indebted to MM. Chevillot and Edwards for a consistent explanation of these phenomena\*. They demonstrated that the peroxide of manganese, when fused with potassa, absorbs oxygen from the atmosphere, and is thereby converted into an acid, the *manganesic*, which unites with the alkali. They attributed the different changes of colour above mentioned to the combination of this acid with different proportions of potassa. By evaporating the red solution rapidly, they succeeded in obtaining a manganesiate of potassa in the form of small prismatic crystals of a purple colour. This salt yields oxygen to combustible substances with great facility, and detonates powerfully with phosphorus. It is decomposed when in solution by very slight causes, being converted into the deutoxide of manganese.

The subsequent researches of Dr. Forchhammer render it probable that the green and red colours are produced by two acids, the *manganeseous* and *manganesic*, the former giving rise to the green, and the latter to the red. He succeeded in forming a solution of *manganesic acid* in the following manner. A mixture of the nitrate of baryta was heated with the peroxide of manganese, by which means the manganesite of baryta was generated; and to this salt, after having been well washed with water, a quantity of dilute sulphuric acid was added, precisely sufficient for combining with its base. The *manganeseous acid*, at the moment of being set free, resolving itself into the deutoxide of manganese and *manganesic acid*, and the latter, dissolving in the water, formed a beautiful red solution. Dr. Forchhammer infers from his analysis of these compounds, that the *manganeseous acid* contains three and the *manganesic* four atoms of oxygen united with one atom of manganese. (*Annals of Philosophy*, vol. xvi.)

*Chloride of Manganese*.—This compound is made by heating the muriate of manganese in a glass vessel from which the atmospheric

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\* An. de Ch. et de Ph. vol. viii.

air is excluded. It fuses readily at a red heat, and forms a pink-coloured lamellated mass on cooling. It is deliquescent, and of course very soluble in water, being converted by that fluid, with evolution of caloric, into the muriate of manganese. According to the analysis of Dr J. Davy it contains 36 parts of chlorine and 30.6 of manganese\*; but Dr Thomson states the quantity of manganese at 28.

The *protosulphuret* of *manganese* may be procured by igniting the sulphate with one-sixth of its weight of charcoal in powder.—(Berthier.) It is also formed by the action of sulphuretted hydrogen on the protosulphate at a red heat.—Arfwedson in An. of Phil. vol. vii. N. S.) It occurs native in Cornwall and at Nagyag in Transylvania. It dissolves completely in dilute sulphuric or muriatic acid, with disengagement of very pure sulphuretted hydrogen.

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## SECTION XII.

### IRON.

Iron has a peculiar gray colour, and strong metallic lustre, which is susceptible of being heightened by polishing. In ductility and malleability it is inferior to several metals, but it exceeds them all in tenacity. (Page 222.) At common temperatures it is very hard and unyielding, and its hardness may be increased by being heated and then suddenly cooled; but it is at the same time rendered brittle. When heated to redness it is remarkably soft and pliable, so that it may be beaten into any form, or be intimately incorporated or *welded* with another piece of red-hot iron by hammering. Its texture is fibrous, and its specific gravity 7.78. In its pure state it is exceedingly infusible, requiring for fusion a temperature of 158° of Wedgwood's pyrometer. It is attracted by the magnet, and may itself be rendered permanently magnetic by several processes;—a property of great interest and importance, and which is possessed by no other metal excepting cobalt and nickel.

The existence of pure native iron is as yet questionable; for all the masses of meteoric iron hitherto examined contain nickel and cobalt. (Stromeyer.) Metallic iron is easily procured by heating the native oxide with charcoal; but when thus obtained it is never quite free from carbonaceous matter. The only method of preparing iron absolutely pure, is by passing dry hydrogen gas over the pure oxide heated to redness in a tube of porcelain.

Iron has a strong affinity for oxygen. In a perfectly dry atmosphere it undergoes hardly any change; but when moisture is likewise present, it oxidizes or *rusts* in the course of a few days. Heated to redness in the open air, it absorbs oxygen rapidly, and is converted into black scales, called the *black oxide* of iron; and in an atmosphere of oxygen gas it burns with vivid scintillations.

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\* Philosophical Transactions for 1812.

## Oxides of Iron.

Iron combines with oxygen in two proportions only, forming the blue or protoxide, and the red or peroxide of iron. Both these compounds are capable of yielding regular crystallizable salts with acids.

*Protoxide.*—This oxide is the base of the native carbonate of iron, and of the green vitriol of commerce. Its existence was inferred some years ago by Gay-Lussac; (An. de Ch. vol. lxxx.) but Stromeyer first obtained it in an insulated form by passing dry hydrogen gas over the peroxide of iron at a very low temperature. (Edinburgh Journal of Science. No. x.)

The protoxide of iron has a dark blue colour, and when melted with vitreous substances communicates to them a tint of blue. It is attracted by the magnet, though less powerfully than metallic iron. It is exceedingly combustible; for when fully exposed to air at common temperatures, it suddenly takes fire and burns vividly, being reconverted into the peroxide. Its salts, particularly when in solution, absorb oxygen from the atmosphere with such rapidity that they may even be employed in eudiometry. This protoxide is always formed with evolution of hydrogen gas when metallic iron is put into dilute sulphuric or muriatic acid; and its composition may be determined by collecting and measuring the gas which is disengaged. According to Gay-Lussac it is composed of 8 parts of oxygen, and 28.3 parts of iron; but Dr Thomson infers from an analysis of the protosulphate of iron, that the quantity of iron united with 5 parts of oxygen is 28 precisely. The atomic weight of the protoxide is therefore 36.

The protoxide of iron is precipitated as a white hydrate by pure alkalies, as a white carbonate by alkaline carbonates, and as a white ferrocyanate by ferrocyanate of potassa. The two former precipitates become first green and then red, and the latter green and blue by exposure to the air. The solution of gall-nuts produces no change of colour. Sulphuretted hydrogen does not act if the protoxide is united with any of the stronger acids; but the alkaline hydrosulphurets cause a black precipitate, the protosulphuret of iron.

*Peroxide.*—The red or peroxide is a natural product, known to mineralogists under the name of *red hematite*. It sometimes occurs massive, at other times fibrous, and occasionally in the form of beautiful rhomboidal crystals. It may be made chemically by dissolving iron in nitro-muriatic acid, and adding an alkali. The hydrate of the red oxide of a brownish-red colour subsides, which is identical in composition with the mineral called *brown hematite*, and consists of 10 parts or one atom of the peroxide, and 9 parts or one atom of water.

The peroxide of iron is not attracted by the magnet. Fused with vitreous substances it communicates to them a red or yellow colour. It combines with most of the acids, forming salts, the greater number of which are red. Its presence may be detected by very decisive tests. The pure alkalies, fixed or volatile, precipitate it as the hydrate. The alkaline carbonates have a similar effect, for the peroxide of iron does not form a permanent salt with carbonic acid. With the ferrocyanate of potassa it forms Prussian blue, the ferrocyanate of the peroxide of iron. The sulphocyanate of potassa causes a deep blood-red, and infusion of gall-nuts, a black colour. Sulphuretted hydrogen converts the peroxide into the protoxide of iron, and a deposition of sulphur takes place at the same time. These re-agents, and especially

the ferrocyanate and sulphocyanate of potassa afford an unerring test of the presence of minute quantities of the peroxide of iron. On this account it is customary, in testing for iron, to convert it into the peroxide, which is easily effected by boiling the solution with a small quantity of nitric acid.

The researches of several chemists, such as Gay-Lussac, Berzelius, Bucholz, and Thomson, leave no doubt that the oxygen contained in the blue and red oxides of iron is in the ratio of one to one and a half. Consequently, the peroxide consists of 28 parts or one atom of iron and 12 parts or an atom and a half of oxygen. (Page 98.)

*Black oxide.*—The substance, long supposed to be the protoxide of iron, contains more oxygen than the blue, and less than the red oxide. It cannot be regarded as a definite compound of iron and oxygen; but is composed of the two real oxides united in a proportion which is by no means constant. It occurs native, frequently crystallized in the form of a regular octahedron, which is not only attracted by the magnet, but is itself sometimes magnetic. It is always formed when iron is heated to redness in the open air; and is likewise generated by the contact of watery vapour with iron at a red heat. The composition of the product, however, varies with the duration of the process and the temperature which is employed. Thus, according to Bucholz, Berzelius, and Thomson, 100 parts of iron, when oxidized by steam, unite with nearly 30 of oxygen; whereas in a similar experiment performed by Gay-Lussac, 37.8 parts of oxygen were absorbed. The oxide of Gay-Lussac may be regarded as a compound of one atom of the protoxide and two atoms of the peroxide; and Berzelius is of opinion that the composition of magnetic iron ore is similar.

The nature of the black oxide is further elucidated by the action of acids. On digesting the black oxide in sulphuric acid, an olive-coloured solution is formed, containing two salts, sulphate of the peroxide and protoxide, which may be separated from each other by alcohol. (Proust and Gay-Lussac.) These mixed salts give green precipitates with alkalies, and a very deep blue ink with an infusion of gall-nuts.

The black oxide of iron is the cause of the dull green colour of bottle glass.

*Chlorides of iron.*—Chlorine unites in two proportions with iron, forming compounds which were described in 1812 by Dr John Davy. The protochloride is made by evaporating a solution of the protomuriate to dryness, and heating it to redness in a glass tube from which the air is excluded. The resulting chloride has a gray colour, a lamellated texture, and metallic lustre. It is composed of one atom of each element, and is converted by water into the protomuriate of iron.

The perchloride is formed by burning iron wire in an atmosphere of chlorine. It is of a bright yellowish-brown colour, crystallizes in small iridescent plates, and is volatile at a temperature a little above 212° F. It consists of one atom of iron and an atom and a half of chlorine, and forms with water a red-coloured solution, which is the permuriate of iron.

An iodide of iron may be formed by heating iron in the vapour of iodine. It is converted by water into the hydriodate.

*Sulphurets of iron.*—There are two compounds of iron and sulphur, both of which are natural products. The protosulphuret is the magnetic iron pyrites of mineralogists. It is a brittle yellow substance, of a metallic lustre, and is feebly attracted by the magnet. By exposure to air and moisture, it is gradually converted into the protosulphate of

iron. It may be made artificially by igniting the protosulphate of iron with charcoal; or still more conveniently by heating a mixture of iron filings and sulphur. (Page 201.) It is dissolved completely and readily by dilute sulphuric or muriatic acid, with disengagement of sulphuretted hydrogen. It is composed of one atom of iron and one atom of sulphur.

The bisulphuret, which contains two atoms of sulphur, is the common iron pyrites. When heated to redness, it loses half its sulphur, and is converted into the protosulphuret. It is insoluble in sulphuric and muriatic acid.

*Phosphuret of iron.*—This compound may be formed by heating the phosphate of iron with charcoal. It is sometimes contained in metallic iron, to the properties of which it is exceedingly injurious by causing it to be brittle at common temperatures.

*Carburets of iron.*—Carbon and iron unite in very various proportions; but there are four compounds which are distinct from one another, namely, cast or pig iron, steel, cast steel, and graphite or plumbago.

The native oxides of iron, which commonly contain argillaceous and siliceous substances, are reduced to the metallic state by the action of coke or charcoal and lime at a high temperature. The oxygen of the oxide of iron unites with one portion of carbon, and the metal with another, yielding carbonic acid and carburet of iron; while the earthy substances together with a little oxide of iron enter into combination, forming a vitreous substance called *slag*, which rises to the surface. The fused carburet is then drawn off by an aperture at the bottom of the furnace, and received in hollows or moulds made with sand. In this state it is neither ductile nor malleable, but very brittle; and fuses with such facility at a red heat that it cannot be welded. It is highly crystalline, and its texture is granular. It contains about 1-13d of its weight of carbon, together with small quantities of manganese, calcium, silicium, and probably aluminum; and besides these substances, which are chemically combined with the iron, particles of charcoal, earthy matters, and unreduced ore, are frequently inclosed within it.

Cast iron is converted into malleable iron by exposure in a reverberatory furnace to the combined action of air and intense heat. During this process all the decomposed ore is reduced, earthy matters rise to the surface as slag, and the carbon is oxidized. As the purity of the iron increases, its fusibility diminishes, until at length, though the temperature remains the same, the iron becomes solid. It is then subjected, while still hot, to the operation of rolling or hammering, by which its particles are approximated. The metal, thus procured, is no longer a carburet, but is the purest iron of commerce. It is not, however, absolutely pure; for Berzelius has detected in it about one-half per cent. of carbon, and it likewise appears to contain silicium.

Steel is made by exposing bars of the purest malleable iron, surrounded with charcoal in powder, to a long-continued red heat. During this process the iron unites with about 1-150th of its weight of carbon, and acquires new properties. In ductility and malleability it is far inferior to iron; but exceeds it greatly in hardness, sonorousness, and elasticity. Its texture is more compact than that of iron, and it is susceptible of a far higher polish. It bears a strong red heat without entering into fusion, and may be welded with iron. When combined with an additional quantity of carbon, it forms cast steel. In this state it is harder and more elastic, has a closer texture, and re-



ceives a higher polish than common steel. It is so fusible, however, that it cannot be welded.

Steel differs chemically from cast iron in being composed of purer iron, and in containing a smaller proportion of carbon. It is readily distinguished from malleable iron by the action of an acid. When a drop of dilute muriatic acid is placed on steel, a black spot appears, in consequence of a portion of iron being dissolved, while the charcoal is left.

Graphite, more commonly known under the name of plumbago or black lead, is a native carburet of iron, which contains 95 per cent. of carbon. It is unchangeable in the air, and like pure charcoal is attacked with difficulty by chemical substances. It has an iron-gray colour, metallic lustre, and granular texture. Its chief use is in making pencils and crucibles, and in burnishing iron to protect it from rust.

## SECTION XIII.

### ZINC.—CADMIUM.

#### *Zinc.*

The zinc of commerce, sometimes called *spelter*, is obtained either from *calamine* the native carbonate of zinc, or from the native sulphuret, the *zinc blende* of mineralogists. It is procured from the former by heat and carbonaceous matters; and from the latter by a similar process after the ore has been previously oxidized by *roasting*, that is, by exposure to the air at a low red heat. When first extracted from its ores it is never quite pure; but contains charcoal, sulphur, and several metals in small quantity. It may be freed from these impurities by distillation,—by exposing it to a white heat in an earthen retort, to which a receiver full of water is adapted.

Zinc has a strong metallic lustre, and a bluish-white colour. Its texture is lamellated, and its density about 7. It is a hard metal, being acted on by the file with difficulty. At low or high degrees of heat it is brittle; but at temperatures between 210° and 300° F., it is both malleable and ductile. It fuses at 680° F., and when slowly cooled assumes regular forms. Exposed in close vessels to a white heat, it sublimes unchanged.

Zinc undergoes little change by the action of air and moisture. When fused in open vessels it absorbs oxygen, and forms the white oxide, called *flowers* of zinc. Heated to full redness in a covered crucible, it burns into flame as soon as the cover is removed, and burns with a brilliant white light. The combustion ensues with such violence, that the oxide as it is formed is mechanically carried up into the air. Zinc is readily oxidized by dilute sulphuric or muriatic acid, and the hydrogen which is evolved contains a small quantity of metallic zinc in combination.

*Oxide of zinc.*—Chemists are acquainted with one compound only of zinc and oxygen, and this oxide is formed under all the circumstances just mentioned. At common temperatures it is white; but when heated to low redness, it assumes a yellow colour, which gradually dis-

appears on cooling. It is quite fixed in the fire. It is insoluble in water, and therefore does not affect the blue colour of plants; but it is a strong salifiable base, forming regular salts with acids, most of which are colourless. It combines also with some of the alkalies. According to the analysis of Dr Thomson it is composed of

Zinc	.	34	.	.	one atom.
Oxygen	.	8	.	.	one atom.

And hence 42 is its combining proportion.

The presence of zinc is easily recognised by the following characters.—The oxide is precipitated from its solutions as a white hydrate by pure potassa or ammonia, and as carbonate by carbonate of ammonia, but is completely redissolved by an excess of the precipitant. The fixed alkaline carbonates precipitate it permanently as the carbonate of zinc. Hydrosulphuret of ammonia causes a white precipitate, which is either a hydrosulphuret of the oxide of zinc, or a hydrated sulphuret of the metal. Sulphuretted hydrogen acts in a similar manner, if the solution is quite neutral; but it has no effect if an excess of any strong acid is present.

The *Chloride or butter of Zinc* was made by Dr J. Davy by evaporating the muriate to dryness and then heating it to redness in a glass tube. It deliquesces on exposure to the air, being reconverted into a muriate. It is composed of one atom of chlorine and one atom of zinc.

The native sulphuret of zinc, or zinc blende, is frequently found in dodecahedral crystals, or in forms allied to the dodecahedron. Its structure is lamellated, its lustre adamantine, and its colour variable, being sometimes yellow, red, brown, or black. It may be made artificially by heating to redness a mixture of oxide of zinc and sulphur, by decomposing the sulphate of zinc by charcoal, or by drying the white precipitate obtained on adding the hydrosulphuret of ammonia to a salt of zinc.

The sulphuret of zinc is composed of one atom of each of its constituents, and is dissolved with disengagement of sulphuretted hydrogen by dilute muriatic or sulphuric acid.

### Cadmium.

Cadmium was discovered in 1817 by Stromeyer in an oxide of zinc which had been prepared for medical purposes\*; and he has since found it in several of the ores of that metal, especially in a radiated blende from Bohemia which contains about five per cent. of cadmium. The late Dr Clarke detected its existence in some of the zinc ores of Derbyshire, and in the common zinc of commerce. Mr Herapath has found it in considerable quantity in the zinc works near Bristol†. During the reduction of calamine by coal, the cadmium, which is very volatile, flies off in vapour mixed with soot and some oxide of zinc, and collects in the roof of the vault, just above the tube leading from the crucible. Some portions of this substance yielded from twelve to twenty per cent. of cadmium.

The process by which Stromeyer separates cadmium from zinc or other metals is the following. The ore of cadmium is dissolved in

\* Annals of Philosophy, vol. xiv.

† Ibid. N.S. vol. iii.

dilute sulphuric or muriatic acid, and after adding a portion of free acid, a current of sulphuretted hydrogen gas is transmitted through the liquid, by means of which the cadmium is precipitated as sulphuret, while the zinc continues in solution. The sulphuret of cadmium is then decomposed by nitric acid, and the solution evaporated to dryness. The dry nitrate of cadmium is dissolved in water, and an excess of carbonate of ammonia is added. The white carbonate of cadmium subsides, which, when heated to redness, yields a pure oxide. By mixing this oxide with charcoal, and exposing the mixture to a red heat, metallic cadmium sublimes.

A very elegant process for separating zinc from cadmium was proposed by Dr Wollaston. The solution of the mixed metals is put into a platinum capsule, and a piece of metallic zinc is placed in it. If cadmium is present, it is reduced, and adheres so tenaciously to the capsule, that it may be washed with water without danger of being lost. It may then be dissolved either by nitric or dilute muriatic acid.

Cadmium, in colour and lustre, has a strong resemblance to tin, but is somewhat harder and more tenacious. It is very ductile and malleable. Its specific gravity is 8.604 before being hammered, and 8.694 afterwards. It melts at about the same temperature as tin, and is nearly as volatile as mercury, condensing like it into globules which have a metallic lustre. Its vapour has no odour.

When heated in the open air, it absorbs oxygen, and is converted into an oxide. Cadmium is readily oxidized and dissolved by nitric acid, which is its proper solvent. Sulphuric and muriatic acids act upon it less easily, and the oxygen is then derived from water.

Cadmium combines with oxygen, so far as is yet known, in one proportion only; and this oxide is conveniently procured in a separate state by igniting the carbonate. It has an orange colour, and is fixed in the fire. It is insoluble in water, and does not change the colour of violets; but it is a powerful salifiable base, forming neutral salts with acids. This oxide, according to the analysis of Stromeyer, is composed of 56 parts of cadmium and 8 parts of oxygen. It is of course regarded as a compound of one atom of each element, and consequently 56 is the atomic weight of cadmium.

The oxide of cadmium is precipitated as a white hydrate by pure ammonia, but is redissolved by excess of the alkali. It is precipitated permanently by pure potassa as a hydrate, and by all the alkaline carbonates as carbonate of cadmium.

The sulphuret of cadmium, which occurs native in some kinds of zinc blende, is easily procured by the action of sulphuretted hydrogen on a salt of cadmium. It has a yellowish orange colour, and is distinguished from the sulphuret of arsenic by being insoluble in pure potassa, and by sustaining a white heat without subliming. It is composed of 56 parts or one atom of cadmium and 16 parts or one atom of sulphur. (Stromeyer.)

The chloride of cadmium may be prepared by decomposing the muriate by heat.

## SECTION XIV.

## TIN.

The tin of commerce, known by the names of block and grain tin, is procured from the native oxide by means of heat and charcoal. The best grain tin is almost chemically pure, containing, according to Dr Thomson, very minute quantities of copper and iron, and occasionally of arsenic.

Tin has a white colour, and a lustre resembling that of silver. The brilliancy of its surface is soon impaired by exposure to the atmosphere, though it is not oxidized even by the combined agency of air and moisture. Its malleability is very considerable; for the thickness of common tin-foil does not exceed 1-1000th of an inch. In ductility and tenacity it is inferior to several metals. It is soft and inelastic, and when bent backwards and forwards, emits a peculiar crackling noise. Its specific gravity is about 7.9. At 442 F. it fuses, and if exposed at the same time to the air, its surface tarnishes, and a gray powder is formed. When heated to whiteness, it takes fire and burns with a white flame, being converted into the peroxide of tin.

*Oxides of Tin.*—Tin is susceptible of two degrees of oxidation. Both the oxides of tin form salts by uniting with acids; but they are likewise capable of combining with alkalies. From data furnished by the experiments of Berzelius, Gay-Lussac, and Thomson, these oxides are inferred to be thus constituted:—

	<i>Tin.</i>	<i>Oxygen.</i>
Protoxide	58 or one atom.	8 or one atom.
Peroxide	58 . . .	16 or two atoms.

The protoxide is of a gray colour, and is formed when tin is kept for some time in a state of fusion in an open vessel. It may also be procured by precipitation from the protomuriate of tin. This salt is made by boiling tin in strong muriatic acid, when the metal is oxidized by the decomposition of water; and if atmospheric air be carefully excluded, a pure protomuriate results. From this solution the hydrate of the protoxide may be precipitated either by pure potassa or the carbonate of that alkali; but an excess of the former must be carefully avoided, as otherwise the precipitate would be redissolved. It is essential likewise to the success of the process that the protoxide should be both washed and dried without being exposed to the air.

The protoxide of tin is remarkable for its powerful affinity for oxygen. When heated in open vessels, it is converted into the peroxide with evolution of heat and light. Its salts not only attract oxygen from the air, but act as powerful deoxidizing agents. Thus the protomuriate of tin converts the peroxide of copper or iron into protoxides, and it precipitates silver, mercury, and platinum from their solutions in the metallic state. Added to a solution of gold, it occasions a purple-coloured precipitate, the *purple of Cassius*, which is a compound of the peroxide of tin and the protoxide of gold. By this character the protoxide of tin is recognised with certainty. It is thrown down by sulphuretted hydrogen as the black protosulphuret of tin.

The peroxide of tin is most conveniently prepared by the action of nitric acid on metallic tin. Nitric acid, in its most concentrated state,

does not act easily upon tin; but when a small quantity of water is added, violent effervescence takes place owing to the evolution of nitrous acid and the deutoxide of nitrogen, and a white powder, the hydrated peroxide, is produced. On edulcorating this substance, and heating it to redness, watery vapour is expelled, and the pure peroxide, of a straw yellow colour, remains. In this process ammonia is generated, a circumstance which proves water as well as nitric acid to have been decomposed.

The peroxide of tin has a very feeble affinity for acids. With nitric acid it does not unite at all; and as prepared by the preceding method, it is dissolved by muriatic acid, even before being ignited, with great difficulty. The permuriate of tin may however be formed by the action of nitro-muriatic acid on metallic tin, aided by a gentle heat. In this manner is obtained the solution of tin employed as a mordant in dyeing.

The peroxide of tin is separated from its solution in muriatic acid as a bulky hydrate by potassa, ammonia, or the alkaline carbonates, and the precipitate is easily and completely redissolved by the pure fixed alkali in excess. Sulphuretted hydrogen occasions a yellow precipitate, which is either the hydrosulphuret of the peroxide of tin, or the bisulphuret of the metal.

The peroxide of tin, when melted with glass, forms white enamel.

*Chlorides of Tin.*—Tin unites in two proportions with chlorine, and the researches of Dr Davy leave no doubt of these compounds being analogous in composition to the oxides of tin.

The protochloride, which consists of one atom of tin and one atom of chlorine, may be made either by evaporating the muriate of the protoxide to dryness and fusing the residue in a close vessel, or by heating an amalgam of tin with calomel. (Dr Davy.) It is a gray solid substance, of a resinous lustre, which fuses at a heat below redness, and when heated in chlorine gas is converted into the bichloride.

The bichloride, composed of one atom of tin and two atoms of chlorine, may be prepared either by heating metallic tin or the protochloride in an atmosphere of chlorine, or by distilling a mixture of eight parts of tin in powder with twenty-four of corrosive sublimate. It is a colourless volatile liquid, which emits copious white fumes when exposed to the atmosphere. It has a very strong attraction for water, and is converted by that fluid into the permuriate. It was formerly called the *fuming liquor* of Libavius.

*Sulphurets of Tin.*—The protosulphuret is best formed by heating sulphur with metallic tin. A brittle compound of a bluish gray colour and metallic lustre results, which is fusible at a red heat, and assumes a lamellated structure in cooling. It is dissolved by muriatic acid, with disengagement of sulphuretted hydrogen. According to the analysis of Dr Davy and Berzelius, it is composed of one atom of tin and one atom of sulphur.

The bisulphuret, formerly called *aurum musivum*, has a golden yellow colour, and is made by heating a mixture of sulphur and the oxide of tin in close vessels. The elements of the latter unite with separate portions of sulphur, forming sulphurous acid and bisulphuret of tin. This compound was supposed by Proust to be the hydrosulphuret of the peroxide of tin, and its real nature was first made known by Dr Davy. (Philos. Trans. for 1812, page 198.) It consists of one atom of tin and two atoms of sulphur.

By exposing a mixture of sulphur and the protosulphuret of tin to a



low red heat, Berzelius obtained a compound consisting of 58 parts or one atom of tin, and 24 parts or one atom and a half of sulphur. If it is really a definite compound, it should be termed a *sesquisulphuret*.

## SECTION XV.

### ARSENIC.

Metallic arsenic sometimes occurs native, but more frequently it is found in combination with other metals, and especially with cobalt and iron. On roasting these arsenical ores in a reverberating furnace, the arsenic, from its volatility, is expelled, combines with oxygen as it rises, and condenses into thick cakes on the roof of the chimney. The sublimed mass, after being purified by a second sublimation, is the virulent poison known by the name of *arsenic* or *white oxide of arsenic*. From this substance the metal itself is procured by heating it with charcoal.

Arsenic is an exceedingly brittle metal, of a strong metallic lustre, and white colour, running into steel gray. Its structure is crystalline, and its density 8.3. When heated to 356° F. it sublimes without previously liquefying; for its point of fusion is far above that of its sublimation, and has not hitherto been determined. Its vapour has a strong odour of garlic, a property which is possessed by no other metal, and therefore forms a distinguishing character for metallic arsenic\*. In close vessels it may be sublimed without change, but if atmospheric air is admitted, it is rapidly converted into the white oxide. It soon tarnishes by exposure to the atmosphere at common temperatures, acquiring a dark film upon its surface. This crust, which is exceedingly superficial, was supposed by Berzelius to be a distinct oxide; but it is more generally regarded as a mixture of white oxide and metallic arsenic.

### Compounds of Arsenic and Oxygen.

Chemists are acquainted with two compounds of arsenic and oxygen, and as they both possess the properties of an acid, the terms *arsenious* and *arsenic acid* have been properly applied to them. Considerable difference of opinion exists as to their composition. Berzelius maintains that the oxygen of the former is to that of the latter as 3 to 5, while Dr Thomson contends that the ratio is as 2 to 3. To decide the question between these eminent analysts, an appeal to direct experiment by other chemists is necessary. According to Dr Thomson, whose data are more generally adopted in this country than those of Berzelius, 38 is the atomic weight of arsenic, and its two acids are thus constituted:—

	Arsenic.	Oxygen.
Arsenious acid .	38 or one atom.	16 or two atoms.
Arsenic acid .	38 or one atom.	24 or three atoms.

\* Zinc is said to emit a similar odour when thrown in powder on burning charcoal.

*Arsenious acid*.—This compound, frequently called *white oxide of arsenic*, is always generated when arsenic is heated in open vessels, and may be prepared by digesting the metal in dilute nitric acid. At  $380^{\circ}$  it is volatilized, yielding vapours which do not possess the odour of garlic, and which condense unchanged on cold surfaces. If the sublimation is conducted slowly, the vapour is deposited in the form of distinct octahedral crystals of an adamantine lustre and perfectly transparent. If the arsenious acid is suddenly heated beyond its subliming point, it fuses into a transparent brittle glass, which gradually becomes opaque by keeping. The specific gravity of this glass is about 3.7.

Arsenious acid has an acid taste, followed by an impression of sweetness. (Davy.) It reddens vegetable blue colours feebly, an effect which is best shown by placing the acid in powder on moistened litmus paper. It combines with salifiable bases, forming salts which are termed *arsenites*.

According to the experiments of Klaproth and Bucholz, 1000 parts of boiling water dissolve 77.75 of arsenious acid; and the solution, after having cooled to  $60^{\circ}$  F., contains only 30 parts. The same quantity of water at  $60^{\circ}$  F., when mixed with the acid in powder, dissolves only two parts and a half.

The tests which are commonly recommended for detecting the presence of arsenious acid are four in number; namely, lime water, the ammoniacal nitrate of silver, the ammoniacal sulphate of copper, and sulphuretted hydrogen.

1. When lime water is added in excess to a solution of arsenious acid, a white precipitate subsides, which is the arsenite of lime. On drying this salt, mixing it with powdered charcoal or black flux, and heating the mixture contained in a glass tube to redness by means of a spirit-lamp, the arsenic is reduced, sublimes, and condenses in a cool part of the tube. The process of reduction is absolutely necessary, since several other acids as well as the arsenious, such as the carbonic, phosphoric, oxalic, and tartaric acids, yield white precipitates with lime water. The arsenite of lime is soluble in all acids which are capable of dissolving lime itself. Indeed all the arsenites are dissolved by those acids with which their bases do not form insoluble compounds.

Lime water is of little service for discovering arsenious acid in mixed fluids. For the arsenite of lime is so light a powder, that when formed in gelatinous or oleaginous solutions, such as in broth or tea made with milk, it remains suspended in the liquid, and cannot be separated from it.

2. Arsenious acid is not precipitated by nitrate of silver unless an alkali be present, which may unite with the nitric acid. Ammonia is commonly employed for the purpose; but as the arsenite of silver is very soluble in ammonia, an excess of the alkali might retain the arsenite of silver in solution. To remedy this inconvenience, Mr Hume proposes to employ the ammoniacal nitrate of silver, which is made by dropping ammonia into a solution of lunar caustic till the oxide of silver at first thrown down is nearly all dissolved. The liquid thus prepared contains the precise quantity of ammonia which is required; and when mixed with arsenious acid, two neutral salts result, the soluble nitrate of ammonia, and the insoluble yellow arsenite of silver. The ammoniacal nitrate of silver likewise diminishes the risk of fallacy that might arise from the presence of phosphoric acid. The phosphate of silver

is so very soluble in ammonia, that when a neutral phosphate is mixed with the ammoniacal nitrate of silver, the resulting phosphate of silver is held almost entirely in solution by the free ammonia.

The test of nitrate of silver, however, even in its improved state, is still liable to objection. For when arsenious acid in small proportion is mixed with salts of muriatic acid, or animal and vegetable infusions, the arsenite of silver either does not subside at all, or is precipitated in so impure a state that its characteristic colour cannot be distinguished. Several methods have been proposed for obviating this source of fallacy; but Dr Christison has shown, as I conceive quite satisfactorily, that this test cannot be relied on in practice.

3. The ammoniacal sulphate of copper, which is made by adding sulphate of copper to ammonia till it ceases to be dissolved, occasions with arsenious acid a green precipitate, which has been long used as a pigment under the name of *Scheele's green*. This test, though well adapted for detecting arsenious acid dissolved in pure water, is very fallacious when applied to mixed fluids. Dr Christison has proved that the ammoniacal sulphate of copper produces in some animal and vegetable infusions, containing no arsenic, a greenish precipitate, which may be mistaken for Scheele's green; whereas in other mixed fluids, such as tea and porter, to which arsenic has been previously added, it occasions none at all, if the arsenious acid is in small quantity. In some of these liquids, a free vegetable acid is doubtless the solvent; but the arsenite of copper is also dissolved by tannin and perhaps by other vegetable as well as some animal principles.

4. When a current of sulphuretted hydrogen gas is conducted through a solution of arsenious acid, the fluid immediately acquires a yellow colour, and in a short time becomes turbid, owing to the formation of orpiment, or the yellow sulphuret of arsenic. The precipitate is at first partially suspended in the liquid; but as soon as the free sulphuretted hydrogen is expelled by boiling, it subsides perfectly, and may easily be collected on a filter. One condition, however, must be observed in order to insure success, namely, that the liquid does not contain a free alkali, for the sulphuret of arsenic is dissolved with remarkable facility by pure potassa or ammonia. To avoid this source of fallacy, it is necessary to acidulate the solution with a little acetic or muriatic acid. Sulphuretted hydrogen likewise acts on arsenic in all vegetable and animal fluids if previously boiled, filtered, and acidulated.

But it does not necessarily follow, because sulphuretted hydrogen causes a yellow precipitate, that arsenic is present; for there are no less than four other substances, namely, selenium, cadmium, tin, and antimony, the sulphurets of which, judging from their colour alone, might be mistaken for orpiment. From these and all other substances whatever, the sulphuret of arsenic may be thus distinguished — When heated with black flux in the manner described for reducing the arsenite of lime, a metallic crust of an iron-gray colour externally, and crystalline on its inner surface, is deposited on the cool part of the tube; and by converting a portion of this crust into vapour, its alliaceous odour will instantly be perceived. Besides these circumstances, which alone are quite satisfactory, it is easy to procure additional evidence by reconvertng the metal into arsenious acid, so as to obtain it in the form of resplendent octahedral crystals. This is done by holding that part of the tube to which the arsenic adheres about three-fourths of an inch above a very small spirit-lamp flame, so that the

metal may be slowly sublimed. As it rises in vapour it combines with oxygen, and is deposited in crystals within the tube. The character of these crystals with respect to volatility, lustre, transparency, and form, is so exceedingly well marked, that a practised eye may safely identify them, though their weight should not exceed the 100th part of a grain. This experiment does not succeed unless the tube be quite clean and dry.

It hence appears, that of the various tests for arsenic, the only one which gives uniform results, and is applicable to every case, is sulphuretted hydrogen:—all the rest may be dispensed with. For this great improvement in the mode of testing for arsenious acid, we are indebted to Dr Christison. By this process he discovered the presence of arsenious acid when mixed with complex fluids, such as tea, porter, and the like, in the proportion of one-fourth of a grain to an ounce; and more recently he has twice obtained so small quantity as the 20th of a grain from the stomachs of people who had been poisoned with arsenic. (Edinburgh Medical and Surgical Journal for October 1824; and second volume of the Transactions of the Medico-Chirurgical Society of Edinburgh.)

The black flux employed in the processes for reducing arsenic, is prepared by deflagrating a mixture of the bitartrate of potassa with half its weight of nitre. The nitric and tartaric acids undergo decomposition, and the solid product is pure carbonate of potassa and charcoal. When this substance is employed in the reduction of arsenious acid or its salts, the charcoal is of course the chief ingredient; but the alkali is of use in retaining the arsenious acid until the temperature is sufficiently high for its decomposition. With sulphuret of arsenic, on the contrary, the alkali is the active ingredient, the potassium of which unites with sulphur and liberates the arsenic; but the charcoal operates usefully by facilitating the decomposition of the alkaline carbonate.

*Arsenic acid.*—This compound is made by dissolving the arsenious acid in concentrated nitre, mixed with a little muriatic acid, and distilling the solution to perfect dryness. The acid, thus prepared, has a sour metallic taste, reddens vegetable blue colours, and with alkalis forms neutral salts, which are termed *arseniates*. It is much more soluble in water than arsenious acid, dissolving in five or six times its weight of cold, and in a still smaller quantity of hot water. It forms irregular grains when its solution is evaporated, but does not crystallize. If strongly heated it fuses into a glass which is deliquescent. When urged by a very strong red heat it is converted into oxygen and arsenious acid. It is an active poison.

Arsenic acid is slowly reconverted by sulphuretted hydrogen gas into arsenious acid, and is then precipitated as orpiment. The soluble arseniates, when mixed with the nitrates of lead or silver, form insoluble arseniates, the former of which has a white, and the latter a brick-red colour. They dissolve readily in dilute nitric acid, and when heated with charcoal yield metallic arsenic.

*Chloride of Arsenic.*—When arsenic in powder is thrown into a jar full of dry chlorine gas, it takes fire, and a chloride of arsenic is generated; and the same compound may be formed by distilling a mixture of six parts of corrosive sublimate with one of arsenic. It is a colourless volatile liquid, which fumes strongly on exposure to the air, hence called *fuming liquor of arsenic*, and is resolved by water into muriatic and arsenious acids. According to Dr J. Davy it is composed of 60.48 parts of chlorine and 39.52 of arsenic, a proportion which does

not correspond with the laws of combination, and therefore is doubtless inexact.

*Arseniuretted hydrogen.*—This gas, which was discovered by Scheele, is most conveniently prepared by digesting an alloy of tin and arsenic in muriatic acid. It is a colourless elastic fluid, of a fetid odour, resembling that of garlic. Its specific gravity is about 0.5. It extinguishes bodies in combustion, but is itself kindled by them, and burns with a blue flame. It instantly destroys small animals that are immersed in it, and is poisonous in a high degree, having proved fatal to a German philosopher, the late M. Gehlen. With oxygen gas it forms an explosive mixture, and is decomposed by chlorine with deposition of arsenic. It is not absorbed by water, nor does it possess acid properties. It has not hitherto been obtained in a pure state, being always mixed with hydrogen, and consequently its composition has not been exactly determined.

A solid compound of arsenic and hydrogen of a brownish colour was discovered by Sir H. Davy, and Gay-Lussac and Thénard. It is formed by the action of water on an alloy of potassium and arsenic; and it is also generated by attaching a piece of arsenic to the negative wire during the decompositions of water by a galvanic battery. Its composition is unknown.

*Sulphurets of Arsenic.*—Sulphur unites with arsenic in two proportions, forming compounds which are known by the names of *realgar* and *orpiment*. They both occur native, and may be made artificially by heating mixtures of arsenious acid and sulphur, the nature of the product depending on the quantity of sulphur employed. They are both fusible by heat, and may be sublimed in close vessels without change. Realgar, which is the protosulphuret, is of a red colour, and is composed of 38 parts or one atom of metallic arsenic, and 16 or one atom of sulphur. Orpiment has a rich yellow colour, and consists of 38 parts or one atom of arsenic, and 24 parts or an atom and a half of sulphur. It is therefore a *sesquisulphuret* of arsenic. Berzelius has proved that the precipitate formed by the action of sulphuretted hydrogen on a solution of arsenious acid, is constituted in a similar manner.

Orpiment is employed as a pigment, and is the colouring principle of the paint called *King's yellow*. M. Braconnot has proposed it likewise for dyeing silk, woollen or cotton stuffs of a yellow colour. For this purpose the cloth is soaked in a solution of orpiment in ammonia, and then suspended in a warm apartment. The alkali evaporates, and leaves the orpiment permanently attached to the fibres of the cloth. (*An. de Ch. et de Ph.* vol. xii.)

The experiments of Orfila have proved that the sulphurets of arsenic are poisonous, though in a much less degree than arsenious acid. The precipitated sulphuret is more injurious than native orpiment.



## SECTION XVI.

CHROMIUM. MOLYBDENUM. TUNGSTEN. CO-  
LUMBIUM.

## Chromium.

Chromium\* was discovered in 1797 by Vauquelin†, in a beautiful red mineral, the native chromate of lead. It has since been detected in the mineral called *chromate of iron*, a compound of the oxides of chromium and iron, which occurs abundantly in several parts of the continent, in America, and at Unst in Shetland. (Hibbert.)

Chromium, which has hitherto been procured in very small quantity, owing to its powerful attraction for oxygen, may be obtained by exposing the oxide of chromium mixed with charcoal to the most intense heat of a smith's forge. It is a brittle metal, of a greyish white colour, and very infusible. Its specific gravity is 5.9.

Chromium unites with oxygen in three proportions, forming two oxides and one acid, the constitution of which has not hitherto been determined by direct experiment. Dr Thomson has proved, however, that the equivalent of chromic acid is 52, so that on the probable assumption of its being composed of one atom of chromium and three atoms of oxygen, 28 must be the atomic weight of the metal. According to these data, the composition of the oxides and acid of chromium may be thus stated.

	Chromium.	Oxygen.
Protoxide .	28 or one atom .	8 or one atom.
Deutoxide .	28 . . .	16 two atoms.
Chromic acid	28 . . .	24 three atoms.

*Protoxide.*—This oxide is easily prepared by dissolving the chromate of potassa in water, and mixing it with a solution of the proto-nitrate of mercury, when an orange-coloured precipitate, the chromate of the protoxide of mercury, subsides. On heating this salt to redness in an earthen crucible, the mercury is dissipated in vapour, and the chromic acid is resolved into oxygen and the protoxide of chromium.

The protoxide of chromium is of a green colour, exceedingly infusible, and suffers no change by heat. It is insoluble in water, and after being strongly heated, resists the action of the most powerful acids. Deflagrated with nitre, it is oxidized to its maximum, and is thus reconverted into chromic acid. Fused with borax or vitreous substances, it communicates to them a beautiful green colour, a property which affords an excellent test of its presence, and renders it exceedingly useful in the arts. The emerald owes its colour to the presence of this oxide.

The protoxide of chromium is a salifiable base, and its salts, which

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\* From *Χρῶμα* colour, indicative of its remarkable tendency to form coloured compounds.

† Annales de Chimie, vol. xxv. and lxx.

have a green colour, may be easily prepared in the following manner. To a boiling solution of the chromate of potassa in water, equal measures of strong muriatic acid and alcohol are added in successive small portions, until the red tint of the chromic acid disappears entirely, and the liquid acquires a pure green colour. On pouring an excess of pure ammonia into this solution, a pale green bulky precipitate is formed, which consists of one atom of the protoxide and 26 atoms of water. (Thomson.) The hydrate is readily dissolved by acids.

*Deutoxide.*—The brown or deutoxide of chromium is formed by exposing the nitrate of the protoxide to a temperature precisely sufficient for decomposing the nitric acid. It has not hitherto been studied with care.

*Chromic acid.*—This acid is prepared by digesting the chromate of baryta in a quantity of dilute sulphuric acid exactly sufficient for combining with the baryta. The sulphate of baryta subsides, and a solution of chromic acid is obtained.

Chromic acid has a dark ruby-red colour, and forms irregular crystals when its solution is concentrated. It is very soluble in water, has a sour taste, and possesses all the properties of an acid. It is converted into the green oxide, with evolution of oxygen, by exposure to a strong heat. It yields a muriate of the protoxide when boiled with muriatic acid and alcohol, and the direct solar rays have a similar effect when muriatic acid is present. With sulphurous acid it forms a sulphate of the protoxide.

Chromic acid is characterized by its colour, and by forming coloured salts with alkaline bases. The most important of these salts is the chromate of lead, which is found native in small quantity, and is easily prepared by mixing the chromate of potassa with a soluble salt of lead. It is of a rich yellow colour, and is employed in the arts of painting and dyeing to great extent.

*Fluo-chromic acid gas.*—When a mixture of fluor-spar and chromate of lead is distilled with fuming or even common sulphuric acid in a leaden retort, a red-coloured gas is disengaged, which is composed of fluoric and chromic acids. This gas acts rapidly upon glass, with deposition of chromic acid and formation of fluo-silicic acid gas. It is absorbed by water, and the solution is found to contain a mixture of fluoric and chromic acids. The watery vapour of the atmosphere effects its decomposition, so that when mixed with air, red fumes appear, owing to the separation of minute crystals of chromic acid. This gas may be regarded as a compound of fluorine and chromium, a view which is rendered very plausible by the circumstance of its being decomposed so readily by moisture.

*Chlorochromic acid gas.*—This compound is formed by the action of fuming sulphuric acid on a mixture of chromate of lead and chloride of sodium. It is a red-coloured gas, which may be collected in glass vessels over mercury. It is decomposed instantly by water, and yields a solution of muriatic and chromic acids. It may be regarded either as a compound of muriatic and chromic acids, or of chlorine and chromium.

These gases were discovered in the year 1825 by M. Unverdorben. (Edinburgh Journal of Science, No. vii.)

## Molybdenum.

When the native sulphuret of molybdenum, in fine powder, is di-

gested in nitro-muriatic acid until the ore is completely decomposed, and the residue is briskly heated, in order to expel sulphuric acid, molybdic acid remains in the form of a white heavy powder. From this acid metallic molybdenum may be obtained by exposing it with charcoal to the strongest heat of a smith's forge; or by conducting over it a current of hydrogen gas while strongly heated in a tube of porcelain. (Berzelius.)

Molybdenum is a brittle metal, very infusible, and of a white colour. It has hitherto been procured in small quantities only, and its properties are known imperfectly. When heated in open vessels it absorbs oxygen, and is converted into *molybdic acid*; and the same compound is generated by the action of chlorine or nitro-muriatic acid. It has three degrees of oxidation, forming two oxides and one acid. The molybdic acid, according to Bucholz, is composed of 48 parts of molybdenum, and 24 parts of oxygen; and consequently, on the supposition that this acid contains three atoms of oxygen, 48 is the atomic weight of the metal itself.

Molybdic acid is a white powder, of specific gravity 3.4. It has a sharp metallic taste, reddens litmus paper, and forms salts with alkaline bases. It is very sparingly soluble in water; but the molybdates of potassa, soda, and ammonia, dissolve in that fluid, and the molybdic acid is precipitated from the solutions by any of the strong acids.

Berzelius has lately described the two oxides of molybdenum. (Edinburgh Journal of Science. No. vii.) The *protoxide* is black, and consists of one atom of oxygen and one atom of molybdenum. The *deutoxide* is brown, and contains twice as much oxygen as the protoxide. They both form salts with acids. Berzelius states that the blue *molybdous acid* of Bucholz, is a bimolybdate of the deutoxide of molybdenum.

Berzelius has likewise succeeded in forming three *chlorides* of molybdenum, the composition of which is analogous to the compounds of this metal with oxygen.

The native *sulphuret* of molybdenum, according to the analysis of Bucholz, is composed of 48 parts or one atom of molybdenum, and 32 parts or two atoms of sulphur. Berzelius has lately discovered another sulphuret, of a ruby-red colour, transparent, and crystallized. It is proportional to the molybdic acid; that is, contains three atoms of sulphur to one atom of the metal.

## Tungsten.

Tungsten may be procured in the metallic state by exposing tungstic acid, mixed with charcoal, to intense heat. It has a grayish white colour and considerable brilliancy. Its density is 17.4. It is one of the most infusible of the metals, and is nearly equal to steel in hardness. When heated in the open air, or digested in nitric acid, oxidation ensues, and it is converted into *tungstic acid*.

Chemists are acquainted with two compounds of this metal and oxygen, namely, the *dark-brown oxide*, and the *yellow acid of tungsten*; and according to the analyses of Berzelius, (An. de Ch. et de Ph. vol. xvii.) the oxygen of the former is to that of the latter in the ratio of two to three. It is hence inferred, that the real protoxide of tungsten is yet unknown, and that tungstic acid contains three atoms of oxygen to one atom of the metal. Now, Bucholz ascertained that

this acid consists of 96 parts of tungsten and 24 parts of oxygen, and consequently 96 is the atomic weight of tungsten, and 120 the equivalent of its acid.

A convenient method of preparing tungstic acid is by digesting the native tungstate of lime, very finely levigated, in nitric acid; by which means the nitrate of lime is formed, and the tungstic acid separated in the form of a yellow powder. Long digestion is required before all the lime is removed; but the process is facilitated by acting upon the mineral alternately by nitric acid and ammonia. The tungstic acid is dissolved readily by that alkali, and may be obtained in a separate state by heating the tungstate of ammonia to redness. Tungstic acid may also be prepared by the action of muriatic acid on *Wolfram*, the native tungstate of iron and manganese.

Tungstic acid is of a yellow colour, is insoluble in water, and has no effect on litmus paper. With alkaline bases it forms salts called *tungstates*, which are decomposed by the stronger acids. When strongly heated in open vessels it acquires a green colour, and becomes blue when exposed to the action of hydrogen gas at a temperature of 500° or 600° F. According to Berzelius, these changes of colour are not connected with any change of composition. By hydrogen gas at a red heat the tungstic acid is converted into the dark brown oxide.

The compounds of tungsten with the other simple substances possess little interest.

### Columbium.

This metal was discovered in 1801 by Mr Hatchett, who detected it in a black mineral belonging to the British Museum, supposed to have come from Massachusetts in North America, and, from this circumstance, applied to it the name of *columbium*. About two years after, M. Ekeberg, a Swedish chemist, extracted the same substance from *tantalite* and *ytthro-tantalite*; and, on the supposition of its being different from columbium, described it under the name of *tantalum*. The identity of these metals, however, was established in 1809 by Dr Wollaston.

Columbium exists in its ores as an acid, united either with the oxides of iron and manganese, as in *tantalite*, or with the earth *yttria*, as in the *ytthro-tantalite*. This acid is obtained by fusing its ore with three or four times its weight of carbonate of potassa, when a soluble columbate of that alkali results, from which columbic acid is precipitated as a white hydrate by acids.

The hydrated columbic acid is tasteless, and insoluble in water; but when placed on moistened litmus paper, it communicates a red tinge. It is dissolved by the sulphuric, muriatic, and some vegetable acids; but it does not diminish their acidity, or appear to form definite compounds with them. With alkalis it unites readily; and though it does not neutralize their properties completely, crystallized salts may be obtained by evaporation. When the hydrated acid is heated to redness, water is expelled, and the anhydrous columbic acid remains. In this state it is attacked by alkalis only.

According to the analyses of Berzelius and Dr Thomson, 144 is the atomic weight of columbium, and columbic acid is composed of one atom of the metal and one atom of oxygen.

When columbic acid is exposed to the united agency of charcoal and intense heat, it is reduced to the metallic state, a process which

was first successfully performed by Berzelius. Columbium is a brittle metal, of an iron-gray colour, and metallic lustre. It is not attacked by the nitric, muriatic, or nitro-muriatic acids; but is converted into the acid by being heated with potassa or nitre. The same product is formed when it is heated in open vessels.

Columbium has hitherto been obtained in very minute quantity.

## SECTION XVII.

### ANTIMONY.

Antimony sometimes occurs native; but its only ore which is abundant, and from which the antimony of commerce is derived, is the sulphuret. This sulphuret was long regarded as the metal itself, and was called *antimony* or *crude antimony*; while the pure metal was termed the *regulus of antimony*.

Metallic antimony may be obtained either by heating the native sulphuret in a covered crucible with half its weight of iron filings, or by mixing it with two-thirds of its weight of cream of tartar and one-third of nitre, and throwing the mixture, in small successive portions, into a red hot crucible. By the first process the sulphur unites with iron, and in the second it is expelled in the form of sulphurous acid; while the fused antimony, which in both cases collects at the bottom of the crucible, may be drawn off and received in moulds. The antimony, thus obtained, is not absolutely pure; and therefore, for chemical purposes, should be procured by heating the oxide with an equal weight of cream of tartar.

Antimony is a brittle metal, of a white colour running into bluish-gray, and is possessed of considerable lustre. Its density is about 6.7. At 810° F. it fuses; and, when slowly cooled, sometimes crystallizes in octahedral or dodecahedral crystals. Its structure is highly lamellated. It has the character of being a volatile metal; but Thénard found that it bears an intense white heat without subliming, provided atmospheric air be perfectly excluded, and no gaseous matters, such as carbonic acid or watery vapour, be disengaged during the process. Its surface tarnishes by exposure to the atmosphere; and by the continued action of air and moisture, a dark matter is formed, which Berzelius regards as a definite compound. It appears, however, to be merely a mixture of the real protoxide and metallic antimony. Heated to whiteness in a covered crucible, and then suddenly exposed to the air, it inflames, and burns with a white light.

The chemists who have paid most attention to the oxides of antimony are Thénard\*, Proust†, Berzelius‡, and Thomson§. The former maintained the existence of six, the second of two, the third of four, and the last of three oxides of antimony. The opinion of Dr Thomson is now admitted by most chemists; and there is reason to believe that

\* An. de Chimie, vol. xxxii. † Journal de Physique, vol. lv.

‡ An. de Chimie, vol. lxxxiii; and An. de Ch. et de Ph. vol. xvii.

§ First Principles, vol. ii.



the proportions which he has assigned to these oxides are very near the truth.

	<i>Antimony.</i>	<i>Oxygen.</i>
Protoxide	. 44, or one atom,	. 8, = 52
Deutoxide	. 44,	. 12, = 56
Peroxide	. 44,	. 16, = 60

*Protoxide*.—When the muriate of the protoxide of antimony, made by boiling the sulphuret in muriatic acid, (page 201,) is poured into water, a white curdy precipitate, formerly called *powder of Algaroth*, subsides, which is a submuriate of the protoxide. On digesting this salt in a dilute solution of potassa, and then edulcorating it with water, the protoxide is obtained in a state of purity. It may also be procured directly, by adding the carbonate of potassa or soda to a solution of tartar emetic.

The protoxide of antimony is of a dirty white colour. Heated to dull redness in close vessels it fuses without undergoing any other change, and forms an opaque crystalline mass on cooling; but in a strong heat it sublimes. At a red heat in open vessels it absorbs oxygen, and is converted into the deutoxide. It is the only oxide of antimony which forms regular salts with acids, and is the base of the medicinal preparation *tartar emetic*, the tartrate of antimony and potassa. Most of its salts, however, are either insoluble in water, or, like the muriate of antimony, are decomposed by it, owing to the affinity of that fluid for the acid being greater than that of the acid for the oxide of antimony. This oxide is therefore a feeble base; and, indeed, possesses the property of uniting with alkalies. To the foregoing remark, however, the tartrate of antimony and potassa is an exception; for it dissolves readily in water without change. By excess of tartaric or muriatic acid, the insoluble salts of antimony may be rendered soluble in water.

The presence of antimony in solution is easily detected by sulphuretted hydrogen. This gas occasions an orange-coloured precipitate, the hydrated protosulphuret of antimony, which is soluble in pure potassa, and is dissolved with disengagement of sulphuretted hydrogen by hot muriatic acid, forming a solution from which the white submuriate is precipitated by water.

*Deutoxide*. When antimony burns, or is strongly heated in open vessels, the deutoxide is generated, sublimes, and condenses on cold surfaces in the form of acicular crystals of silvery whiteness, formerly called *argentine flowers of antimony*. This oxide does not fuse readily, but is more volatile than the protoxide. It is quite insoluble in water, and in the anhydrous state is attacked with great difficulty by acids. It combines with alkalies, and for this reason it has been called *antimonious acid*, and its salts *antimonites*, by Berzelius. The antimonious acid is precipitated from these salts by acids as a hydrate, which reddens litmus paper, and is dissolved by muriatic acid, though without appearing to form with it a definite compound.

The *peroxide* of antimony, or *antimonic acid*, is obtained as a white hydrate, either by digesting the metal in strong nitric acid, or by dissolving it in nitro-muriatic acid and throwing the solution into water. When recently precipitated it reddens litmus paper, and may be dissolved in water, by means of muriatic or tartaric acids. It does not enter into definite combination with acids, but with alkalies forms salts, which are called *antimoniates*. When the hydrated peroxide is

exposed to a temperature of  $500^{\circ}$  or  $600^{\circ}$  F. the water is evolved, and the pure peroxide of a yellow colour remains. In this state it resists the action of muriatic acid. When exposed to a red heat, it parts with oxygen, and is converted into the deutoxide.

*Chlorides of antimony.* When antimony in powder is thrown into a jar of chlorine gas, combustion ensues, and the protochloride of antimony is generated. The same compound may be formed by distilling a mixture of antimony with about twice and half its weight of corrosive sublimate, when the volatile chloride of antimony passes over into the recipient, and metallic mercury remains in the retort. At common temperatures it is a soft solid, thence called *butter of antimony*, which is liquefied by gentle heat, and crystallizes on cooling. It deliquesces on exposure to the air; and when mixed with water, is converted into muriatic acid and the protoxide of antimony. If a large quantity of water is employed, the whole of the oxide subsides as the submuriate.

The bichloride is generated by passing dry chlorine gas over heated metallic antimony. It is a transparent volatile liquid, which emits fumes on exposure to the air. Mixed with water, it is converted into muriatic acid, and the hydrated peroxide which subsides. It contains twice as much chlorine as the protochloride, or is composed of one atom of antimony, and two atoms of chlorine. (Rose in the *Annals of Philosophy*, N. S. vol. x.)

Dr Thomson, in his "First Principles," has described another chloride of antimony, composed of one atom of chlorine and two atoms of the metal. It is, therefore, a *dichloride*.

*Sulphurets of antimony.* The native sulphuret of antimony is of a lead-gray colour, and though generally compact, sometimes occurs in acicular crystals, or in rhombic prisms. When heated in close vessels, it enters into fusion without undergoing any other change. Boiled in hot muriatic acid, it is dissolved with disengagement of sulphuretted hydrogen. The experiments of Berzelius, Dr Davy, and Thomson, leave no doubt of its being analogous in composition to the protoxide of antimony, that is, consisting of one atom of each of its elements. It may be formed artificially by fusing together antimony and sulphur, or by transmitting a current of sulphuretted hydrogen gas through a solution of tartar emetic. The orange precipitate, which subsides in the last mentioned process, is commonly regarded as the hydrosulphuret of the oxide of antimony. In my opinion it is a hydrated sulphuret of the metal; for when well washed and treated by sulphuric acid it does not yield a trace of sulphuretted hydrogen.

When sulphuret of antimony is boiled in a solution of potassa, a liquid is obtained, from which as it cools, an orange-coloured matter, called *Kermes mineral*, is deposited; and on subsequently neutralizing the cold solution with an acid, an additional quantity of a similar substance, the *golden sulphuret* of the pharmacopœia, subsides. Both these compounds, thus procured, are essentially the same as the hydrated sulphuret above described. The action of the alkali on the sulphuret of antimony admits of a two-fold explanation. It is possible that the latter may be dissolved directly by the former, and that it is again deposited when the alkali is neutralized. It is more probable, however, that the elements of water and the sulphuret of antimony react on one another, forming sulphuretted hydrogen and protoxide of antimony; and that the liquid contains a double salt, composed of one atom of potassa, one atom of the protoxide of antimony, and one of

sulphuretted hydrogen. On neutralizing the potassa with an acid, sulphuretted hydrogen and the protoxide are set at liberty, and by mutual reaction of their elements are reconverted into water and protosulphuret of antimony.

The *sesquisulphuret* is formed, according to M. Rose, by transmitting sulphuretted hydrogen gas through a solution of the deutoxide of antimony in dilute muriatic acid. (Annals of Philosophy, N. S. vol. x.)

M. Rose formed the *bisulphuret*, consisting of one atom of antimony and two atoms of sulphur, by the action of sulphuretted hydrogen on a solution of the peroxide. The golden sulphuret prepared by boiling sulphuret of antimony and sulphur in solution of potassa, a process which is not adopted by either of our Colleges, is a bisulphuret.

M. Rose has likewise demonstrated that the *red antimony* of Mineralogists (*rothspiesglanzerz*) is a compound of one atom of the protoxide combined with two atoms of the protosulphuret of antimony. The pharmaceutic preparations known by the terms of *glass*, *liver*, and *crocus* of antimony, are of a similar nature, though less definite in composition, owing to the mode by which they are prepared. They are made by roasting the native sulphuret, so as to form sulphurous acid and oxide of antimony, and then vitrifying the oxide together with undecomposed ore, by means of a strong heat.

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## SECTION XVIII.

### URANIUM. CERIUM. COBALT. NICKEL.

#### *Uranium.*

Uranium was discovered in 1789 by Klaproth in a mineral of Saxony, called from its black colour *pitchblende*, which consists of the protoxide of uranium and oxide of iron. From this ore the uranium may be conveniently extracted by the following process.—After heating the mineral to redness, and reducing it to fine powder, it is digested in pure nitric acid diluted with three or four parts of water, taking the precaution to employ a larger quantity of the mineral than the nitric acid present can dissolve. By this mode of operating, the protoxide is converted into the peroxide of uranium, which unites with the nitric acid almost to the total exclusion of the iron. A current of sulphuretted hydrogen is then transmitted through the solution, in order to separate lead and copper, the sulphurets of which are always mixed with pitchblende. The solution is boiled to expel the free sulphuretted hydrogen, and after being concentrated by evaporation, is set aside to crystallize. The nitrate of uranium is gradually deposited in flattened four-sided prisms of a beautiful lemon-yellow colour.

The properties of metallic uranium are as yet known imperfectly. It was prepared by Arfwedson, by conducting hydrogen gas over the protoxide of uranium heated in a glass tube. The substance obtained by this process was crystalline, of a metallic lustre, and of a reddish-brown colour. It suffered no change on exposure to air at common temperatures; but when heated in open vessels absorbed oxygen, and

was reconverted into the protoxide. From its lustre it was inferred to be metallic uranium.

Chemists are acquainted with two compounds of uranium and oxygen, the composition of which has been minutely studied by Arfwedson\* and Thomson†. According to the chemist last mentioned, whose experiments are the most recent, the weight of an atom of uranium is 208, and its oxides are composed of

	Uranium.	Oxygen.
Protoxide .	208	8 = 216
Peroxide .	208	16 = 224

According to the analyses of Arfwedson, 216 is the atomic weight of uranium, and the oxygen in its two oxides is in the ratio of 1 to 1.5; and Berzelius, from the composition of three salts of uranium, has arrived at a similar conclusion.

The protoxide of uranium is of a very dark green colour, and is obtained by decomposing the nitrate of the peroxide by heat. It is exceedingly infusible, and bears any temperature hitherto tried without change. It unites with acids, forming salts of a green colour. It is readily oxidized by nitric acid, and yields a yellow solution which is a nitrate of the peroxide. The protoxide is employed in the arts for giving a black colour to porcelain.

The peroxide of uranium is of a yellow or orange colour, and most of its salts have a similar tint. It not only combines with acids, but likewise unites with alkaline bases, a property which was first noticed by Arfwedson. It is precipitated from acids as a yellow hydrate by pure alkalies, fixed or volatile; but retains a portion of these bases in combination. It is thrown down as a carbonate by the carbonate of soda or ammonia, and is redissolved by an excess of the precipitant, a circumstance which affords an easy method of separating uranium from iron. It is not precipitated by sulphuretted hydrogen. With ferrocyanate of potassa it gives a brownish-red precipitate, not unlike the ferrocyanate of the peroxide of copper.

The peroxide of uranium is decomposed by a strong heat, and converted into the protoxide. From its affinity for alkalies, it is difficult to obtain it in a state of perfect purity. It is employed in the arts for giving an orange colour to porcelain.

## Cerium.

Cerium was discovered in 1803 by MM. Hisinger and Berzelius, in a rare Swedish mineral known by the name of cerite, and its existence was recognised about the same time by Klaproth. Dr Thomson has since found it to the extent of thirty-four per cent. in a mineral from Greenland, called *Allanite*, in honour of Mr Allan, who first distinguished it as a distinct species.

The properties of cerium are in a great measure unknown. It appears from the experiments of Vauquelin, who obtained it in minute buttons not larger than the head of a pin, that it is a white brittle metal, which resists the action of nitric, but is dissolved by nitro-muriatic acid. According to an experiment made by Mr Children and Dr

\* Annals of Philosophy, N. S. vol. vii. † First Principles, vol. ii.

Thomson, metallic cerium is volatile in very intense degrees of heat. (*Annals of Philosophy*, vol. ii.)

*Oxides of Cerium.*—Cerium unites with oxygen in two proportions, and the composition of the resulting oxides has been particularly studied by M. Hisinger\*. Dr Thomson† has likewise made experiments on the subject, and infers from data furnished partly by himself and partly by M. Hisinger, that 50 is the atomic weight of cerium, and that its oxides are thus constituted—

	Cerium.	Oxygen.
Protoxide	50	8 = 58
Deutoxide	50	12 = 62

The protoxide of cerium is a white powder, which is insoluble in water, and forms salts with acids, all of which, if soluble, have an acid reaction. Exposed to the air at common temperatures it suffers no change; but if heated in open vessels, it absorbs oxygen and is converted into the peroxide. It is precipitated from its salts as a white hydrate by pure alkalies; as a white carbonate by alkaline carbonates, but is redissolved by the precipitant in excess; and as a white oxalate by the oxalate of ammonia.

The peroxide of cerium is of a fawn-red colour. It is dissolved by several of the acids, but is a weaker base than the protoxide. Digested in muriatic acid, chlorine is disengaged and a protomuriate results.

The most convenient method of extracting pure oxide of cerium from cerite, is by the process of Laugier. After reducing the cerite to powder, it is dissolved in nitro-muriatic acid, and the solution is evaporated to perfect dryness. The soluble parts are then redissolved by water, and an excess of ammonia is added. The precipitate thus formed, consisting of the oxides of iron and cerium, is well washed and afterwards digested in a solution of oxalic acid, which dissolves the iron, and forms an insoluble oxalate with the cerium. By heating this oxalate to redness in an open fire, the acid is decomposed, and the peroxide of cerium is obtained in a pure state.

## Cobalt.

This metal is met with in the earth chiefly in combination with arsenic, constituting an ore from which all the cobalt of commerce is derived. It is a constant ingredient of meteoric iron; at least Professor Stromeyer informs me that he has analyzed several varieties, in every one of which he has detected the presence of cobalt.

When the native arseniuret of cobalt is broken into small pieces, and exposed in a reverberatory furnace to the united action of heat and air, its elements are oxidized, most of the arsenious acid is expelled in the form of vapour, and an impure oxide of cobalt, called *zaffre*, remains. On heating this substance with a mixture of sand and potash, a beautiful blue-coloured glass is obtained, which, when reduced to powder, is known by the name of *smalt*.

Metallic cobalt may be obtained by dissolving *zaffre* in muriatic acid, and transmitting through the solution a current of sulphuretted hydrogen gas until the arsenious acid is completely separated in the form of sulphuret of arsenic. The filtered liquid is then boiled with a little

\* *Annals of Philosophy*, vol. iv.

† *First Principles*, vol. i.



nitric acid, in order to convert the protoxide into the peroxide of iron, and an excess of the carbonate of potassa is added. The precipitate, consisting of the peroxide of iron and carbonate of cobalt, after being well washed with water, is digested in a solution of oxalic acid, which dissolves the iron and leaves the cobalt in the form of an insoluble oxalate. (Laugier.) On heating the oxalate of cobalt in a retort from which the atmospheric air is excluded, a large quantity of carbonic acid is evolved, and a black powder, metallic cobalt, is left. (Thomson in *Annals of Philosophy*, N. S. i.) The pure metal is easily procured also by passing a current of dry hydrogen gas over the oxide of cobalt heated to redness in a tube of porcelain.

Cobalt is a brittle metal, of a reddish-gray colour, and weak metallic lustre. Its density is 8.538. It fuses at about  $130^{\circ}$  of Wedgwood, and when slowly cooled it crystallizes. It is attracted by the magnet, and is susceptible of being rendered permanently magnetic. It undergoes little change in the air, but absorbs oxygen when heated in open vessels. It is attacked with difficulty by sulphuric or muriatic acid, but is readily oxidized by means of nitric acid.

*Oxides of Cobalt.*—Chemists are acquainted with two oxides of cobalt. According to the experiments of Rothoff\*, the protoxide is composed of 29.5 parts of cobalt and 8 parts of oxygen, so that the atomic weight of cobalt is 29.5. Dr Thomson, on the contrary, infers from his analysis of the sulphate of cobalt, that 26 is the equivalent of this metal. From this discordance it is clear that the atomic weight of cobalt is not yet known with certainty. According to Rothoff, the oxygen contained in the two oxides is as 1 to 1.5.

The protoxide is of an ash-gray colour, and is the basis of the salts of cobalt, most of which are of a pink hue. When heated to redness in open vessels it absorbs oxygen, and is converted into the peroxide. It may be prepared by decomposing the carbonate of cobalt by heat in a vessel from which the atmospheric air is excluded. It is easily recognised by giving a blue tint to borax when melted with it; and is employed in the arts, in the form of smalt, for communicating a similar colour to glass, earthenware, and porcelain.

The protoxide of cobalt is precipitated from its salts by pure potassa as a blue hydrate, which absorbs oxygen from the air, and gradually becomes black. Pure ammonia, likewise, causes a blue precipitate, which is redissolved by the alkali if in excess. It is thrown down as a pale pink carbonate by the carbonates of potassa, soda, or ammonia; but an excess of the last redissolves it with facility. Sulphuretted hydrogen produces no change, unless the solution is quite neutral, or the oxide is combined with a weak acid. Alkaline hydrosulphurets always precipitate is as the black sulphuret of cobalt.

The muriate of cobalt is celebrated as a sympathetic ink. When diluted with water so as to form a pale pink solution, and then employed as ink, the letters, which are invisible in the cold, become blue if gently heated.

The peroxide of cobalt is of a black colour, and is easily formed from the protoxide in the way already mentioned. It does not unite with acids; and when digested in muriatic acid, the protomuriate of cobalt is generated with disengagement of chlorine. When strongly

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\* *Annals of Philosophy*, vol. iii. p. 356.

heated in close vessels, it gives off oxygen, and is converted into the protoxide.

The compounds of cobalt with the other non-metallic bodies have hitherto been little examined.

### Nickel.

Nickel is a constituent of meteoric iron. It occurs likewise in the copper coloured mineral of Westphalia, termed *copper-nickel*, a native arseniuret of nickel, which in addition to its chief constituents contains sulphur, iron, cobalt, and copper. From this mineral the oxalate of nickel may be prepared by a process precisely similar to that described for forming the oxalate of cobalt. The only difficulty in preparing nickel consists in separating it from cobalt, and on this subject the reader may consult the essay of M. Laugier. (*An. de Ch. et de Ph.* vol. ix.)

Metallic nickel, which may be prepared either by heating the oxalate in close vessels, or by the combined action of heat and charcoal or hydrogen on the oxide of nickel, is of a white colour, intermediate between that of tin and silver. It has a strong metallic lustre, and is both ductile and malleable. It is attracted by the magnet, and like iron and cobalt may be rendered magnetic. Its specific gravity after fusion is about 8.279, and is increased to near 9.0 by hammering.

Nickel is exceedingly infusible, even more so than pure iron. It suffers no change at common temperatures by exposure to air and moisture; but absorbs oxygen at a red heat, though not rapidly, and is partially oxidized. The muriatic and sulphuric acids act upon it with difficulty. By the nitric acid it is readily oxidized, and forms a nitrate of the protoxide of nickel.

Nickel is susceptible of two stages of oxidation. The composition of its oxides is stated very differently by different chemists. According to the experiments of Rothoff and Tupputi, 29.5 is the atomic weight of nickel. Thomson estimates it at 26; and Lassaigne at 40. (*An. de Ch. et de Ph.* vol. xvi.) Lassaigne, whose analyses are the most recent, attributes this discordance to the presence of cobalt in the nickel employed by preceding chemists, a supposition which is by no means improbable. According to his experiments, the two oxides are thus constituted.—

	Nickel.	Oxygen.
Protoxide	40	8 = 48
Peroxide	40	16 = 56

The protoxide of nickel is of an ash-gray colour, and may be formed by heating the carbonate, oxalate, or nitrate to redness in an open vessel. It is not attracted by the magnet. It is a strong alkaline base, and nearly all its salts have a green tint. It is precipitated as a hydrate of a pale green colour by the pure alkalies, but is redissolved by ammonia in excess; as a pale green carbonate by alkaline carbonates, but is dissolved by an excess of the carbonate of ammonia; as a black sulphuret by alkaline hydrosulphurets. Sulphuretted hydrogen occasions no precipitate, unless the solution is quite neutral, or the oxide is combined with a weak acid.

The peroxide of nickel is of a black colour, and is formed by transmitting chlorine gas through water in which the hydrate of the pro-

toxide is suspended. The peroxide of nickel does not unite with acids, is decomposed by a red heat, and with hot muriatic acid forms a protomuriate with disengagement of chlorine.

## SECTION XIX.

### BISMUTH. TITANIUM. TELLURIUM.

#### *Bismuth.*

Bismuth is found in the earth both native and in combination with other substances, such as sulphur, oxygen, and arsenic. That which is employed in the arts is derived chiefly from native bismuth, and commonly contains small quantities of sulphur, iron and copper. It may be obtained pure for chemical purposes by heating the oxide or subnitrate to redness along with charcoal.

Bismuth has a reddish-white colour and considerable lustre. Its structure is highly lamellated, and when slowly cooled, it crystallizes in octahedrons. Its density is about 10. It is brittle when cold, but may be hammered into plates while warm. At 476° F. it fuses, and sublimes in close vessels at about 30° Wedgwood. It is a less perfect conductor of caloric than most other metals.

Bismuth undergoes little change by exposure to air at common temperatures. When fused in open vessels, its surface becomes covered with a gray film, which is a mixture of metallic bismuth with the oxide of the metal. Heated to its subliming point it burns with a bluish-white flame, and emits copious fumes of the oxide of bismuth. The metal is attacked with difficulty by muriatic or sulphuric acid, but it is readily oxidized and dissolved by nitric acid.

*Oxide of Bismuth.*—This metal unites with oxygen in one proportion only, forming a yellow-coloured oxide, which may be easily produced by heating the subnitrate to redness. At a full red heat it is fused, and yields a transparent yellow glass. At a still higher temperature it is sublimed. It unites with acids, and most of its salts are white. According to the experiments of Dr J. Davy\*, it is composed of 72 parts of bismuth, and 8 parts of oxygen, and therefore 72 is the atomic weight of bismuth, and 80 the equivalent of its oxide. This result is confirmed by the researches of Dr Thomson†.

When the nitrate of bismuth, either in solution, or in crystals, is put into water, a copious precipitate, the subnitrate, of a beautifully white colour subsides, which was formerly called the *magistery of bismuth*. From its whiteness it is sometimes employed as a paint for improving the complexion; but it is an inconvenient pigment, owing to the facility with which it is blackened by sulphuretted hydrogen. If the nitrate with which it is made contains no excess of acid, and a large quantity of water is employed, the whole of the bismuth is separated as a subnitrate.—By this character bismuth may be both distinguished and separated from other metals.

\* Philosophical Transactions for 1812. † First Principles vol. i.

*Chloride of Bismuth.*—When bismuth in fine powder is introduced into chlorine gas, it takes fire, burns with a pale blue light, and is converted into a chloride, formerly termed *butter* of bismuth. It may be prepared conveniently by heating two parts of corrosive sublimate with one of bismuth, and afterwards expelling the excess of the former, together with the metallic mercury, by heat.

The chloride of bismuth is of a grayish-white colour, opaque, and of a granular texture. It fuses at a temperature a little above that at which the metal itself is liquefied, and bears a red heat in close vessels without subliming. (Dr Davy.) From the experiments of Drs Davy and Thomson, it appears to consist of one atom of each of its elements.

*Sulphuret of Bismuth.*—This sulphuret is found native, and may be formed artificially by fusing bismuth with sulphur. It is of a lead-gray colour, and metallic lustre. The experiments of Drs Davy, Thomson, and Lagerhielm\* leave no doubt of its being composed of one atom of bismuth and one atom of sulphur. I apprehend the dark brown precipitate caused by the action of sulphuretted hydrogen on the salts of bismuth is likewise a protosulphuret.

## Titanium.

Titanium was first recognised as a new substance by Mr Gregor of Cornwall, and its existence was afterwards established by Klaproth†. But the properties of the metal were not ascertained in a satisfactory manner until the year 1822, when Dr Wollaston‡ was led to examine some minute crystals which were found in a slag at the bottom of a smelting furnace at the great iron works at Merthyr Tydvil in Wales, and were presented to him by Mr Buckland. These crystals, which have since been found at other iron works, are of a cubic form, and in colour and lustre are like burnished copper. They conduct electricity, and are attracted slightly by the magnet, a property which seems owing to the presence of a minute quantity of iron. Their specific gravity is 5.3; and their hardness is so great, that they scratch a polished surface of rock crystal. They are exceedingly infusible; but when exposed to the united action of heat and air, their surface becomes covered with a purple-coloured film which is an oxide. They resist the action of the nitric and nitromuriatic acids, but are completely oxidized by being strongly heated with nitre. They are then converted into a white substance, which possesses all the properties of the peroxide of titanium. By this character they are proved to be metallic titanium.

*Oxides of titanium.*—This metal has probably two degrees of oxidation. The *protoxide* is of a purple colour, and is supposed to exist pure in the mineral called *Anatase*; but its composition and chemical properties are unknown. The *peroxide* exists in a nearly pure state in the titanite or rutile. The menaccanite in which titanium was originally discovered by Mr Gregor, is a compound of the oxides of titanium, iron, and manganese. The oxide is best prepared from rutile; but as the process is rather complex, owing to the difficulty of

\* Annals of Philosophy, vol. iv.

† Contributions, vol. i.

‡ Philosophical Transactions for the year 1823.

separating it from iron, I shall refer the reader, for an account of it, to an essay on titanium by M. Rose. (An. de Ch. et de Ph. vol. xxiii.)

The oxide of titanium, when pure, is quite white. It is exceedingly infusible and difficult of reduction; and after being once ignited, ceases to be soluble in acids. M. Rose has observed that, like silica, it possesses weak acid properties. Thus he finds that it unites readily with alkalies, and he denies its power of acting as an alkaline base. On this account he proposes for it the name of *titanic acid*.

If previously ignited with carbonate of potassa, the oxide of titanium is soluble in dilute muriatic acid; but it is retained in solution by so feeble an attraction, that it is precipitated merely by boiling. It is likewise thrown down by the pure and carbonated alkalies, both fixed and volatile. A solution of gall-nuts causes an orange-red colour, which is very characteristic of the presence of titanium. When a rod of zinc is suspended in the solution, a purple-coloured powder, probably the protoxide, is precipitated, which is gradually reconverted into the peroxide.

The atomic weight of titanium, as deduced by Dr Thomson from experiments made by M. Rose and by himself, is 24. Titanic acid is inferred, from the same data, to be composed of 24 parts, or one atom of titanium, and 16 parts or two atoms of oxygen.

### Tellurium.

Tellurium is a rare metal, hitherto found only in the gold mines of Transylvania, and even there in very small quantity. Its existence was inferred by Müller in 1782, and fully established in 1798 by Klaproth\*. It occurs in the metallic state, chiefly in combination with gold and silver.

Tellurium has a tin-white colour running into lead-gray, a strong metallic lustre, and lamellated texture. It is very brittle and its density is 6.115. It fuses at a temperature below redness, and at a red heat is volatile. When heated before the blow pipe it takes fire, burns rapidly with a blue flame bordered with green, and is dissipated in gray coloured pungent inodorous fumes. The odour of decayed horse radish is sometimes emitted during the combustion, and was thought by Klaproth to be peculiar to tellurium; but Berzelius ascribes it solely to the presence of selenium.

*Oxide of Tellurium.*—Tellurium is rapidly oxidized by nitric acid, and a soluble nitrate of the oxide results. The oxide is likewise formed during the combustion of the metal. It is of a gray colour, fuses at a red heat, and at a temperature still higher sublimates. When heated before the blow-pipe on charcoal it is decomposed with violence. It has the property of forming salts both with acids and alkalies. It is precipitated from its solution in acids, as a hydrate, by all the alkalies both pure and carbonated; but is redissolved by an excess of the precipitant. Alkaline hydrosulphurets occasion a black precipitate, which is probably a sulphuret of tellurium. It is reduced to the metallic state, and thrown down as a black powder, by insertion of a rod of zinc, tin, antimony, or iron.

According to Berzelius the oxide of tellurium is composed of nearly 32 parts of the metal, and 8 parts of oxygen; so that 32 may be regard-



ed as the atomic weight of tellurium, and 40 of its oxide. This result, however, differs considerably from that of Klaproth, and therefore requires confirmation.

Tellurium unites in one proportion with chlorine, and in two proportions with hydrogen. The most interesting of these compounds is the telluretted hydrogen gas discovered in 1809 by Sir H. Davy. This gas is colourless, has an odour similar to that of sulphuretted hydrogen, and is absorbed by water, forming a claret-coloured solution. As it unites with alkalies, it may be regarded as a feeble acid. It reddens litmus paper at first; but loses this property after being washed with water.

## SECTION XX.

### COPPER.

Native copper is by no means uncommon. It occurs in large amorphous masses in some parts of America, and is sometimes found in octahedral crystals, or in forms allied to the octahedron. The metallic copper of commerce is extracted chiefly from the native sulphuret.

Copper is distinguished from all other metals, titanium excepted, by having a red colour. It receives a considerable lustre by polishing. Its density is 8.78, and is increased by hammering. It is both ductile and malleable, and in tenacity is inferior only to iron. It is hard and elastic, and consequently sonorous. In fusibility it stands between silver and gold. (Page 223.)

Copper undergoes little change in a perfectly dry atmosphere, but is rusted in a short time by exposure to air and moisture, being converted into a green substance, the carbonate of the peroxide of copper. At a red heat it absorbs oxygen, and is converted into the peroxide, which appears in the form of black scales. It is attacked with difficulty by muriatic and sulphuric acids, and not at all by the vegetable acids, if atmospheric air be excluded; but if air has free access, the metal absorbs oxygen with rapidity, the attraction of the acid for the oxide of copper co-operating with that of the copper for oxygen. Nitric acid acts with violence on copper, forming a nitrate of the peroxide. (Page 132.)

*Oxides of Copper.*—The oxides of this metal have been studied by Proust, Chenevix, Dr Davy, and Berzelius, and especially by the former\*. From the labours of these chemists, it appears that there are but two oxides of copper, and that they are thus constituted:—

	Copper.	Oxygen.	
Protoxide . .	64 . . .	8	= 72
Peroxide . .	64 . . .	16	= 80

Consequently, if the first be regarded as a compound of one atom of each element, 64 is the atomic weight of copper.

\* Journal de Physique, vol. lix.

The *red* or *protoxide* occurs native in the form of octahedral crystals, and is found of peculiar beauty in the mines of Cornwall. It may be prepared artificially by mixing 64 parts of metallic copper in a state of fine division with 80 parts of the peroxide, and heating the mixture to redness in a close vessel; or by boiling a solution of the acetate of copper with sugar, when the peroxide is partially deoxidized, and subsides as a red powder.

The protoxide of copper combines with the muriatic, sulphuric, and probably with several other acids, forming salts, most of which are colourless, and from which the protoxide is precipitated as an orange-coloured hydrate by alkalies. They attract oxygen rapidly from the atmosphere, by which they are converted into per-salts. The proto-muriate is easily formed by putting a solution of the per-muriate with free muriatic acid and copper filings into a well-closed glass phial. The protoxide of copper is soluble in ammonia, and the solution is quite colourless. It becomes blue, however, in the space of a minute, by free exposure to air, owing to the formation of the peroxide.

The *peroxide* of copper, the *copper black* of mineralogists, is sometimes found native, being formed by the spontaneous oxidation of other ores of copper. It may be prepared artificially by calcining metallic copper, by precipitation from the per-salts of copper by means of pure potassa, and by heating the nitrate of copper to redness.

The peroxide of copper varies in colour from a dark brown to a bluish-black, according to the mode of formation. It undergoes no change by heat alone, but is readily reduced to the metallic state by heat and combustible matter. It is insoluble in water, and does not affect the vegetable blue colours. It combines with nearly all the acids, and most of its salts have a green or blue tint. It is soluble likewise in ammonia, forming with it a deep blue solution, a property by which the peroxide of copper is distinguished from all other substances.

The peroxide of copper is precipitated by pure potassa as a blue hydrate, which is rendered black by boiling, the hydrate being decomposed at that temperature. Pure ammonia at first throws down a greenish-blue sub-sulphate, which is redissolved by the precipitant in excess, and forms the deep blue ammoniacal sulphate of copper. Alkaline carbonates cause a bluish-green precipitate, the carbonate of copper, which is redissolved by an excess of carbonate of ammonia. It is precipitated as a dark brown sulphuret by sulphuretted hydrogen, and as a reddish-brown ferrocyanate by the ferrocyanate of potassa. The oxide of copper is thrown down of a yellowish-white colour by albumen, and M. Orfila has proved that this compound is inert, so that albumen is an antidote to poisoning by copper.

Copper is separated in the metallic state by a rod of iron or zinc. (Page 225.) The copper thus obtained, after being washed with a dilute solution of muriatic acid, is chemically pure.

The best mode of detecting copper, when supposed to be present in mixed fluids, is by sulphuretted hydrogen. The sulphuret, after being collected, should be placed on a piece of porcelain, and digested in a few drops of nitric acid. A sulphate of copper is formed, which, when evaporated to dryness, strikes the characteristic deep blue on the addition of ammonia.

*Chlorides of Copper.*—The chlorides of copper have been minutely studied by Proust and Dr Davy. From the able researches of these chemists, and especially of the latter, there is no doubt that the two

chlorides are proportional to the two oxides of copper, or that they are composed of

	Copper.	Chlorine.
Protochloride	64	36
Perchloride	64	72

When copper filings are introduced into an atmosphere of chlorine gas, the metal takes fire spontaneously, and both the chlorides are generated.

The *protochloride* may be conveniently prepared by heating copper filings with twice their weight of corrosive sublimate. In this way it was originally made by Mr Boyle, who termed it *resin of copper*, from its resemblance to common resin. Proust procured it by the action of the protomuriate of tin on the permuriate of copper; and also by decomposing the permuriate by heat. He gave it the name of *white muriate of copper*.

The *protochloride* of copper is fusible at a heat just below redness, and bears a red heat in close vessels without subliming. It is insoluble in water, but dissolves in muriatic acid, and is precipitated unchanged by water as a white powder. Its colour varies with the mode of preparation, being white, yellow, or dark brown.

The *perchloride* is best formed by exposing the permuriate of copper to a temperature not exceeding 400° F. (Dr Davy.) It is a pulverulent substance of a yellow colour, deliquesces on exposure to the air, and is reconverted by water into the permuriate. It parts with half its chlorine, when strongly heated, and the *protochloride* of copper is generated.

*Sulphurets of Copper.*—The *protosulphuret* of copper, the *copper glance* of mineralogists, is formed artificially by heating copper filings with a third of its weight of sulphur. The combination is attended with such free disengagement of caloric, that the mass becomes vividly luminous. According to the analysis of Berzelius, it is composed of 64 parts or one atom of copper, and 16 parts or one atom of sulphur.

The *bisulphuret* is a constituent of *copper pyrites*, in which mineral it is combined with the sulphuret of iron. It may be formed artificially by the action of sulphuretted hydrogen on a per-salt of copper. When exposed to a red heat in a close vessel it loses half its sulphur, and is converted into the *proto-sulphuret*.

The compounds of copper with the other non-metallic bodies are of minor interest.

## SECTION XXI.

### LEAD.

Native lead is an exceedingly rare production; but in combination, especially with sulphur, it occurs in large quantity. All the metallic lead of commerce is extracted from the native sulphuret, the *galena* of mineralogists.

Lead has a bluish-gray colour, and when recently cut, a strong me-

tallic lustre, but it soon tarnishes by exposure to the air. Its density is 11.358. It is soft, flexible, and inelastic. It is both malleable and ductile, possessing the former property in particular to a considerable extent. In tenacity, it is inferior to all ductile metals. It fuses at about 612° F., and when slowly cooled forms octahedral crystals. It may be heated to whiteness in close vessels without subliming. Most of the compounds of lead are poisonous.

Lead is not oxidized by the action of air and moisture, and may be kept in distilled water without change. But if placed in water contained in an open vessel, a slow process of oxidation goes forward, and a white crust is formed, which is a carbonate of the protoxide of lead.

Lead absorbs oxygen quickly at high temperatures. When fused in open vessels, a gray film forms upon its surface, which is a mixture of metallic lead and protoxide; and when strongly heated, it is dissipated in fumes of the yellow oxide of lead.

Lead is not attacked by the muriatic or the vegetable acids, though their presence accelerates the absorption of oxygen from the atmosphere in the same manner as with copper. Cold sulphuric acid does not act upon it; but when boiled in that liquid, the lead is slowly oxidized at the expense of the acid. The only proper solvent for lead is the nitric acid. This reagent oxidizes it rapidly, and forms with its oxide a salt which crystallizes in opaque octahedrons by evaporation.

*Oxides of lead.*—Lead has three degrees of oxidation, and the composition of its oxides, as determined with great care by Berzelius\*, is as follows:—

	<i>Lead.</i>	<i>Oxygen.</i>	
Protoxide .	104	8	= 112
Deutoxide .	104	12	= 116
Peroxide .	104	16	= 120

*Protoxide.*—This oxide is prepared on a large scale by collecting the gray film which forms on the surface of melted lead, and exposing it to heat and air until it acquires a uniform yellow colour. In this state it is the *massicot* of commerce; and when partially fused by heat, the term *litharge* is applied to it. As thus procured it is always mixed with the deutoxide. It may be obtained pure by heating the carbonate or nitrate to low redness in a vessel from which atmospheric air is excluded.

The protoxide of lead has a yellow colour, is insoluble in water, fuses at a red heat, and in close vessels is fixed and unchangeable in the fire. Heated with combustible matters it parts with oxygen, and is reduced. From its insolubility it does not change the vegetable colours under common circumstances; but when rendered soluble by a small quantity of acetic acid, it has a distinct alkaline reaction. It unites with acids, and is the base of all the salts of lead. Most of its salts are of a white colour.

The protoxide of lead is precipitated from its solutions by pure alkalis as a white hydrate, which is redissolved by potassa in excess; as a white carbonate, which is the well-known pigment *white lead*, by alkaline carbonates; as a white sulphate by soluble sulphates; as a dark brown sulphuret by sulphuretted hydrogen; and as the yellow iodide of lead by hydriodic acid or hydriodate of potassa.

M. Orfila has proved experimentally that the sulphate of lead, owing to its insolubility, is not poisonous, and therefore the sulphate of magnesia, or any soluble sulphate, renders the active salts of lead inert.

The best method of detecting the presence of lead in wine or other suspected mixed fluids is by means of sulphuretted hydrogen. The sulphuret of lead, after being collected on a filter and washed, is to be digested in nitric acid diluted with twice its weight of water, until the dark colour of the sulphuret disappears. The solution of the nitrate of lead should then be brought to perfect dryness on a watch glass, in order to expel the excess of nitric acid, and the residue be redissolved in a small quantity of cold water. On dropping a particle of the hydriodate of potassa into a portion of this liquid, the yellow iodide of lead will instantly appear.

The protoxide of lead unites readily with earthy substances, forming with them a transparent colourless glass. Owing to this property it is much employed for glazing earthen ware and porcelain. It enters in large quantity into the composition of flint glass, which it renders more fusible, transparent, and uniform.

Lead is separated from its salts in the metallic state by iron or zinc. The best way of demonstrating this fact is by dissolving one part of the acetate of lead in sixteen of water, and suspending a piece of zinc in the solution by means of a thread. The lead is deposited upon the zinc in a peculiar arborescent form, giving rise to the appearance called *arbor saturni*. This is a convenient method of obtaining very pure metallic lead.

*Deutoxide.*—The deutoxide of lead is the *minium* or *red-lead* of commerce, which is employed as a pigment, and in the manufacture of flint glass. It is formed by heating litharge in open vessels, while a current of air is made to play upon its surface.

This oxide does not unite with acids. When heated to redness it gives off pure oxygen gas, and is reconverted into the protoxide. When digested in nitric acid it is resolved into the protoxide and peroxide of lead, the former of which unites with the acid, while the latter remains as an insoluble powder.

*Peroxide.*—This oxide may be obtained by the action of nitric acid on minium, as just mentioned; but the most convenient method of preparing it is by transmitting a current of chlorine gas through a solution of the acetate of lead. In this process the water is decomposed;—its hydrogen uniting with chlorine, and its oxygen with the protoxide of lead, gives rise to muriatic acid and the peroxide of lead.

The peroxide of lead is of a puce colour, and does not unite with acids. It is resolved by a red heat into the protoxide and oxygen gas.

*Chloride of lead.*—This compound, sometimes called *horn lead* or *plumbum corneum*, is slowly formed by the action of chlorine gas on thin plates of lead, and may be obtained more easily by adding muriatic acid or a solution of sea-salt to the acetate or nitrate of lead dissolved in water. This chloride dissolves to a considerable extent in hot water, especially when acidulated with muriatic acid. In solution it is most probably a muriate of the oxide of lead; but in cooling, the chloride separates in the form of small acicular crystals of a white colour. It fuses at a temperature below redness, and forms as it cools a semi-transparent horny mass. It bears a full red heat in close vessels without subliming. According to the analysis of Dr Davy, it is composed of one atom of lead and one atom of chlorine.

The pigment called *mineral* or *patent yellow* is a compound of the



chloride and protoxide of lead. It is prepared for the purposes of the arts by the action of moistened sea-salt on litharge, by which means a portion of the protoxide is converted into chloride of lead, and then fusing the mixture. Soda is set free during this process, and is converted into a carbonate by absorbing carbonic acid from the atmosphere.

The *iodide of lead* is easily formed by mixing a solution of hydriodic acid or hydriodate of potassa with the acetate or nitrate of lead dissolved in water. It is of a rich yellow colour. It is dissolved by boiling water, forming a colourless solution, and is deposited on cooling in yellow crystalline scales of a brilliant lustre. It is composed of one atom of iodine and one atom of lead.

The *sulphuret of lead* may be made artificially, either by heating together lead and sulphur, or by the action of sulphuretted hydrogen on a salt of lead. It is an abundant natural product, well known by the name of galena. It consists of one atom of lead and one atom of sulphur.

## SECTION XXII.

### MERCURY OR QUICKSILVER.

Mercury is found in the native state, but it occurs more commonly in combination with sulphur as cinnabar. From this ore the mercury of commerce may be extracted by heating it with lime or iron filings, by which means the mercury is volatilized and the sulphur retained. As prepared on a large scale it is usually mixed in small quantity with other metals, from which it may be purified by cautious distillation.

Mercury is distinguished from all other metals by being fluid at common temperatures. It has a tin-white colour and strong metallic lustre. It becomes solid at a temperature which is 39 or 40 degrees below Zero of Fahr., and in congealing, evinces a strong tendency to crystallize in octahedrons. It contracts greatly at the moment of congelation; for while its density at 47° F. is 13.545, the specific gravity of frozen mercury is 15.612. When solid it is malleable, and may be cut with a knife. At 660° F. or near that degree, it enters into ebullition, and condenses again on cool surfaces into metallic globules.

Mercury, if quite pure, is not tarnished in the cold by exposure to air and moisture; but if it contain other metals, the amalgam of those metals oxidizes readily, and collects as a film upon its surface. Mercury is said to be oxidized by long agitation in a bottle half full of air, and the oxide so formed was called by Boerhaave *Ethiops per se*; but it is very probable that the oxidation of mercury observed under these circumstances was solely owing to the presence of other metals. When mercury is exposed to air or oxygen gas, while in the form of vapour, it slowly absorbs oxygen, and is converted into the peroxide of mercury.

The only acids that act on mercury are the sulphuric and nitric acids. The former has no action whatever in the cold; but on the application of heat, the mercury is oxidized at the expense of the acid, pure sulphurous acid gas is disengaged, and a sulphate of mercury is generated. (Page 150.) Nitric acid acts energetically upon mercury

both with and without the aid of heat, oxidizing and dissolving it with evolution of the peroxide of nitrogen.

### Oxides of Mercury.

Mercury is susceptible of two stages of oxidation, and both its oxides are capable of forming salts with acids. It appears from the researches of Donovan\* and Selstrom†, whose results are confirmed by the experiment of Dr Thomson, that these oxides are formed in the following proportions:—

	Mercury.	Oxygen.	
Protoxide	200	8	= 208
Peroxide	200	16	= 216

*Protoxide.*—The protoxide of mercury, which is a black powder, insoluble in water, is best prepared by the process recommended by Donovan. This consists in mixing calomel briskly in a mortar with pure potassa in excess, so as to effect its decomposition as rapidly as possible. The protoxide is then to be washed with cold water, and dried spontaneously in a dark place. These precautions are rendered necessary by the tendency of the protoxide to resolve itself into the peroxide and metallic mercury, a change which is easily effected by heat, by the direct solar rays, and even by day-light. It is on this account very difficult to procure the protoxide of mercury in a state of absolute purity.

This oxide is precipitated from its salts, of which the nitrate is the most interesting, as the black protoxide by pure alkalies; as a white carbonate, which soon becomes dark from the loss of carbonic acid, by alkaline carbonates; as calomel by muriatic acid or any soluble muriate; and as the black protosulphuret by sulphuretted hydrogen. Of these tests, the action of muriatic acid is the most characteristic. The oxide is reduced to the metallic state by copper, phosphorous acid, or protomuriate of tin.

*Peroxide.*—This oxide may be formed either by the combined agency of heat and air, as already mentioned, or by dissolving mercury in nitric acid, and exposing the nitrate so formed to a temperature just sufficient for expelling the whole of the nitric acid. It is commonly known by the name of *red precipitate*.

The peroxide of mercury, thus prepared, is commonly in the form of shining crystalline scales of a red colour. It is soluble to a small extent in water, forming a solution which has an acid metallic taste, and communicates a green colour to the blue infusion of violets. When heated to redness, it is converted into metallic mercury and oxygen. Long exposure to light has a similar effect. (Guibourt.)

Some of the neutral salts of this oxide, such as the nitrate and sulphate, are converted by water, especially at a boiling temperature, into insoluble yellow sub-salts, and into soluble colourless super-salts. The oxide is separated from all acids as a red, or when hydratic as a yellow precipitate, by the pure and carbonated fixed alkalies. Ammonia and its carbonate cause a white precipitate, which is a double salt, consisting of one atom of the acid, one atom of the peroxide, and one atom of ammonia. Sulphuretted hydrogen, phosphorous acid, and protomuriate of tin, reduce the peroxide into the protoxide; and when

\* Annals of Philosophy, vol. xiv. † Ibid. vol. iii. p. 355.

added in larger quantity the first throws down a black sulphuret, and the two latter metallic mercury. The oxide is readily reduced by insertion of a rod of copper.

### Chlorides of Mercury.

Mercury unites with chlorine in two proportions; and the researches of Sir H. Davy and Mr Chenevix leave no doubt that these compounds are analogous in composition to the oxides of mercury, that is, are composed of

	Mercury.	Chlorine.	
Protochloride .	200	36	= 236
Bichloride .	200	72	= 272

*Bichloride.*—When mercury is heated in chlorine gas, it takes fire, and burns with a pale red flame, forming the well-known medicinal preparation and virulent poison *corrosive sublimate* or bichloride of mercury. It is prepared for medical purposes by subliming a mixture of the bisulphate of the peroxide of mercury, with the chloride of sodium or sea-salt. The exact quantities required for mutual decomposition are 296 parts or one atom of the bisulphate, to 120 parts or two atoms of the chloride. Thus,

One atom of the bisulphate of mercury consists of	Two atoms of the chloride of sodium consist of
Sulphuric acid . . . 80 or two atoms.	72 or two atoms of chlorine.
Peroxide of mercury 216 or one atom.	48 or two atoms of sodium.
—	—
296	120

and the products are,

One atom of the bichloride of mercury consisting of	Two atoms of the sulphate of soda consisting of
Mercury . . . 200 or one atom.	Sulphuric acid 80 or two atoms.
Chlorine . . . 72 or two atoms.	Soda . . . 64 or two atoms.
—	—
272	144

The bichloride of mercury, when obtained by sublimation, is a semi-transparent colourless substance, of a crystalline texture. It has an acrid, burning taste, but leaves a nauseous metallic flavour on the tongue. Its specific gravity is 5.2. It sublimes at a red heat without change. It requires twenty times its weight of cold, and only twice its weight of boiling water for solution, and is deposited from the latter, as it cools, in the form of prismatic crystals. Strong alcohol and ether dissolve it in the same proportion as boiling water; and it is soluble in half its weight of concentrated muriatic acid at the temperature of 70° Fahr. With the muriates of ammonia, potassa, soda, and several other bases, it enters into combination, forming double salts, which are more soluble than the chloride itself.

The chloride of mercury is probably converted at the moment of being dissolved into a muriate of the peroxide; at least this view may safely be admitted, since alkalies and other reagents act upon it precisely in the same manner as on other per-salts of mercury. Its aqueous solution is gradually decomposed by light, calomel being deposited.

The presence of mercury in a fluid supposed to contain corrosive

sublimate may be detected by concentrating and digesting it with an excess of pure potassa. The oxide of mercury, which subsides, is then sublimed in a small glass tube by means of a spirit-lamp, and obtained in the form of metallic globules. Dr Christison informs me that this and other processes recommended by medical jurists for the detection of corrosive sublimate in mixed fluids, are not altogether satisfactory. He is at present engaged in an inquiry on the subject, and will soon make known the result of his researches.

A very elegant method of detecting the presence of mercury is to place a drop of the suspected liquid on polished gold, and to touch the moistened surface with a piece of iron wire or the point of a pen-knife, when the part touched instantly becomes white, owing to the formation of an amalgam of gold. This process was originally suggested by Mr Sylvester, and has since been simplified by Dr Paris. (Medical Jurisprudence, by Paris and Fonblanque.)

Many animal and vegetable solutions convert the bichloride of mercury into calomel, a portion of muriatic acid being set free at the same time. Some substances effect this change slowly, while others, and especially albumen, produce it in an instant. Thus when a solution of corrosive sublimate is mixed with albumen, a white flocculent precipitate subsides, which M. Orfila has shown to be a compound of calomel and albumen, and which he has proved experimentally to be inert. (Toxicologie, vol. i.) Consequently, a solution of the white of eggs is an antidote to poisoning by corrosive sublimate.

*Protochloride.*—The protochloride of mercury, or *calomel*, is always generated when chlorine comes in contact with mercury at common temperatures. It may be made by precipitation, by mixing muriatic acid or any soluble muriate with a solution of the proto-nitrate of mercury. It is more commonly prepared by sublimation. This is conveniently done by mixing 272 parts or one atom of the bichloride with 200 parts or one atom of mercury, until the metallic globules entirely disappear, and then subliming. When first prepared it is always mixed with some corrosive sublimate, and therefore it should be reduced to powder and well washed before being employed for chemical or medical purposes.

The protochloride of mercury is a rare mineral production, called *horn quicksilver*, which occurs crystallized in quadrangular prisms, terminated by pyramids. When obtained by sublimation it is in semi-transparent crystalline cakes; but as formed by precipitation, it is a white powder. Its density is 7.2. It is distinguished from the bichloride by not being poisonous, by having no taste, and by being exceedingly insoluble in water. Acids have little effect upon it; but pure alkalies decompose it, separating the black protoxide of mercury and uniting with muriatic acid,—products which necessarily imply the decomposition of water. When calomel is boiled in a solution of the muriate of ammonia, it is converted into corrosive sublimate and metallic mercury. Muriate of soda has a similar effect, though in a less degree.

*Iodides of Mercury.*—The protiodide is formed by mixing a solution of the protonitrate of mercury with the hydriodate of potassa; and the deutiodide by the action of the same hydriodate on any per-salt of mercury. The former is yellow, and is composed of one atom of iodine and one atom of mercury. The other is of an exceedingly rich red colour, and may be used with advantage in painting. It contains twice as much iodine as the yellow iodide. Both these compounds

are insoluble in pure water, but are dissolved by a solution of the hydriodate of potassa.

*Cyanuret of Mercury.*—This compound is best prepared by boiling, in any convenient quantity of water, eight parts of finely levigated ferrocyanate of the peroxide of iron, quite pure and well dried on a sand bath, with eleven parts of the peroxide of mercury in powder, until the blue colour of the ferrocyanate entirely disappears. A colourless solution is formed, which, when filtered and concentrated by evaporation, yields crystals of the cyanuret of mercury in the form of quadrangular prisms. In this process, the oxygen of the oxide of mercury unites with the iron and hydrogen of the ferrocyanic acid; while the metallic mercury enters into combination with the cyanogen. The brown insoluble matter is peroxide of iron. Pure ferrocyanate of iron is easily procured by digesting the common Prussian blue of commerce with muriatic acid diluted with ten parts of water, so as to remove the subsulphate of iron and alumina which it commonly contains, and then edulcorating the insoluble ferrocyanate till the free acid is removed. (*Edinburgh Journal of Science*, No. x.)

The cyanuret of mercury, when pure, is colourless and inodorous, has a very disagreeable metallic taste, and is highly poisonous. It does not affect the colour of litmus or turmeric paper. When strongly heated it is converted into cyanogen and metallic mercury. (Page 207.) It is more soluble in hot than in cold water, and dissolves in that liquid without change. The solution has not the characteristic odour of the salts of hydrocyanic acid, (page 209,) nor do alkalies throw down the oxide of mercury. It is composed of 200 parts or one atom of mercury, and 52 parts or two atoms of cyanogen.

*Sulphurets of Mercury.*—The protosulphuret of mercury may be prepared by transmitting a current of sulphuretted hydrogen gas through a dilute solution of the protonitrate of mercury, or through water in which calomel is suspended. It is a black-coloured substance, convertible into the sulphate of mercury by digestion in strong nitric acid. When exposed to heat it is resolved into the bisulphuret and metallic mercury. It is composed of 200 parts or one atom of mercury, and 16 parts or one atom of sulphur.

The bisulphuret is formed by fusing sulphur with about six times its weight of mercury, and subliming in close vessels. When procured by this process it has a red colour, and is known by the name of *fictitious cinnabar*. Its tint is greatly improved by being reduced to powder, in which state it forms the beautiful pigment *vermilion*. It may be obtained in the moist way by pouring a solution of corrosive sublimate into an excess of hydrosulphuret of ammonia. A black precipitate subsides, which acquires the usual red colour of cinnabar when sublimed. I apprehend the black precipitate formed by the action of sulphuretted hydrogen on the cyanuret of mercury, is likewise a bisulphuret. Cinnabar, as already mentioned, occurs native.

When equal parts of sulphur and mercury are triturated together until metallic globules cease to be visible, the dark coloured mass called *Ethiops mineral* results, which Mr Brande has proved to be a mixture of sulphur and the bisulphuret of mercury. (*Journal of Science*, vol. xviii. p. 294.)

Cinnabar is not attacked by alkalies, or any simple acid; but it is dissolved by the nitro-muriatic acid, with formation of sulphuric acid



and the oxide of mercury. M. Guibourt has shown that it is composed of one atom of mercury and two atoms of sulphur\*.

## SECTION XXIII.

### SILVER.

This metal frequently occurs native in silver mines, both massive and in octahedral or cubic crystals. It is also found in combination with several other metals, such as gold, antimony, copper, and arsenic, and with sulphur.

Pure silver may be obtained for chemical purposes by placing a clean piece of copper in a solution of the nitrate of silver, washing the precipitated metal with pure water, and then digesting it in ammonia, in order to remove any adhering copper. It may also be prepared from the chloride of silver, either by exposing that compound mixed with a pure or carbonated alkali to a strong heat in a black-lead crucible, or by conducting over it a current of hydrogen gas when heated to redness in a tube of porcelain.

Silver has the clearest white colour of all the metals, and is susceptible of receiving a lustre surpassed only by polished steel. In malleability and ductility it is inferior only to gold, and its tenacity is considerable. It is very soft when pure, so that it may be cut with a knife. Its density after being hammered is 10.51. At 20° or 22° of Wedgwood's pyrometer it fuses.

Pure silver does not rust by exposure to air and moisture, nor is it oxidized by fusion in open vessels. It appears, indeed, that a film of oxide is formed when melted silver is exposed to a current of air or oxygen gas; but it spontaneously parts with the oxygen as it becomes solid. When silver in the form of leaves or fine wire is intensely heated by means of electricity, galvanism, or the oxy-hydrogen blow-pipe, it burns with vivid scintillations of a greenish white colour.

The only pure acids that act on silver are the sulphuric and nitric acids, by both of which it is oxidized, forming with the first a sulphate, and with the second a nitrate of silver. It is not attacked by sulphuric acid unless by the aid of heat. Nitric acid is its proper solvent, and forms with it a salt, which, in its fused state, is known by the name of *lunar caustic*.

*Oxide of Silver.*—The oxide of silver is best procured by mixing a solution of pure baryta with nitrate of silver dissolved in water. This oxide is of a brown colour, is insoluble in water, and is completely reduced by a red heat. According to Sir H. Davy, it is composed of 110 parts of silver and 8 parts of oxygen; and, therefore, regarding it as the real protoxide, 110 is the atomic weight of silver.

The oxide of silver is separated from its solutions in nitric acid, by pure alkalies and alkaline earths, as the brown oxide, which is redis-

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\* An. de Ch. et de Ph. vol. i. See also some very judicious observations on the paper of M. Guibourt, by Mr Brande, in the Journal of Science, vol. xviii. p. 291.

solved by ammonia in excess; by alkaline carbonates as a white carbonate, which is soluble in an excess of the carbonate of ammonia; as a dark brown sulphuret by sulphuretted hydrogen; and as a white curdy chloride of silver, which is turned violet by light, and is very soluble in ammonia, by muriatic acid or any soluble muriate. By the last character, silver may be both distinguished and separated from other metallic bodies.

Silver is precipitated in the metallic state by most other metals. When mercury is employed for this purpose, the silver assumes a beautiful arborescent appearance, called *arbor Dianæ*. A very good proportion for the experiment is twenty grains of lunar caustic to six drachms or an ounce of water. The silver thus deposited always contains mercury.

When the oxide of silver, recently precipitated by baryta or lime water, and separated from adhering moisture by bibulous paper, is left in contact for ten or twelve hours with a strong solution of ammonia, the greater part of it is dissolved; but a black powder remains which detonates violently from heat or percussion. This substance, which was discovered by Berthollet, (*An. de Chimie*, vol. i.) appears to be a compound of ammonia and oxide of silver; for the products of its detonation are metallic silver, water, and nitrogen gas. It should be made in very small quantity at a time, and dried spontaneously in the air.

On exposing a solution of the oxide of silver in ammonia to the air, its surface becomes covered with a pellicle, which Mr Faraday considers to be an oxide containing less oxygen than that just described. This opinion he has made highly probable; but further experiments are requisite before the existence of this oxide can be regarded as certain.

*Chloride of silver*.—This compound, which sometimes occurs native in silver mines, is always generated when silver is heated in chlorine gas, and may be prepared conveniently by mixing muriatic acid, or any soluble muriate, with a solution of the nitrate of silver. As formed by precipitation it is quite white; but by exposure to the direct solar rays it becomes violet, and almost black, in the course of a few minutes, and a similar effect is slowly produced by diffused daylight. Muriatic acid is set free during this change, and, according to Berthollet, the dark colour is owing to a separation of the oxide of silver. (*Statique Chimique*, vol. i. p. 195.)

The chloride of silver, sometimes called *luna cornea* or *horn silver*, is insoluble in water, and is dissolved very sparingly by the strongest acids; but it is soluble in ammonia. Hyposulphurous acid likewise dissolves it. At a temperature of about 500° F. it fuses, and forms a semitransparent horny mass on cooling. It bears any degree of heat, or even the combined action of pure charcoal and heat, without decomposition; but hydrogen gas decomposes it readily with formation of muriatic acid. According to the experiments of Berzelius and Dr Thomson it is composed of 110 parts or one atom of silver, and 36 parts or one atom of chlorine.

*Iodide of Silver*.—This compound is formed when the hydriodate of potassa is mixed with a solution of the nitrate of silver. It is of a greenish-yellow colour, is insoluble in water and ammonia, and contains one atom of each of its elements.

*Cyanuret of silver* is formed by mixing hydrocyanic acid with nitrate of silver. It is a white curdy substance, similar in appearance to

the chloride of silver, insoluble in water and nitric acid, and soluble in a solution of ammonia. It is decomposed by muriatic acid with formation of hydrocyanic acid and chloride of silver.

*Sulphuret of silver.*—Silver has a strong affinity for sulphur. This metal tarnishes rapidly when exposed to an atmosphere containing sulphuretted hydrogen gas, owing to the formation of a sulphuret. On transmitting a current of sulphuretted hydrogen through a solution of lunar caustic, a dark brown precipitate subsides, which is a sulphuret of silver. The *silver glance* of mineralogists is a similar compound, and the same sulphuret may be prepared by heating thin plates of silver with alternate layers of sulphur.

The sulphuret of silver, according to the experiments of Berzelius, is a compound of 110 parts or one atom of silver, and 16 parts or one atom of sulphur.

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## SECTION XXIV.

### GOLD.

Gold has hitherto been found only in the metallic state, either pure or in combination with other metals. It occurs massive, capillary, in grains, and crystallized in octahedrons and cubes, or their allied forms. It is sometimes found in primary mountains; but more frequently in alluvial depositions, especially among sand in the beds of rivers, having been washed with water out of disintegrated rocks in which it originally existed.

Gold is the only metal which has a yellow colour, a character by which it is distinguished from all other simple metallic bodies. It is capable of receiving a high lustre by polishing, but is inferior in brilliancy to steel, silver, and mercury. In ductility and malleability it exceeds all other metals; (page 222) but it is surpassed by several in tenacity. Its density is 19.3. When pure it is exceedingly soft and flexible. It fuses at 32° of Wedgwood's pyrometer.

Gold may be exposed for ages to air and moisture without change, nor is it oxidized by being kept in a state of fusion in open vessels. When intensely ignited by means of electricity or the oxy-hydrogen blow-pipe, it burns with a greenish-blue flame, and is dissipated in the form of a purple powder, which is supposed to be an oxide.

Gold is not oxidized or dissolved by any of the pure acids; for it may be boiled even in nitric acid without undergoing any change. Its only solvents are chlorine and nitro-muriatic acid; and it appears from the observations of Sir H. Davy that chlorine is the agent in both cases, since the nitro-muriatic acid does not dissolve gold, except when it gives rise to the formation of chlorine. (Page 169.) It is to be inferred, therefore, that the chlorine unites directly with the gold. Whether the resulting solution is really a chloride of the metal, or a muriate of its oxide, generated by the decomposition of water, is uncertain; but from some recent observations of M. Pelletier, which will be mentioned immediately, I conceive the former opinion to be the more probable. There is no inconvenience, however, in regarding it as a muriate, because reagents act upon it as if it were such.

The most convenient method of forming a solution of gold, is to digest fragments of the metal in a mixture, composed of two measures of muriatic and one of nitric acid, until the acid is saturated. The orange-coloured solution is then evaporated to dryness by a regulated heat, in order to expel the free acid without decomposing the residual chloride of gold. On adding water, the chloride is dissolved, forming a neutral solution of a reddish-brown colour.

*Oxides of gold.*—The chemical history of the oxides of gold is as yet very imperfect. Berzelius is of opinion that there are three oxides. His protoxide is obtained by decomposing the protochloride of gold by a solution of pure potassa, and is of a dark green colour. The deutoxide or purple oxide is the product of the combustion of gold. The composition of these oxides has not yet been satisfactorily determined, and the very existence of the first, though probable, may be questioned. The only well-known oxide is that which is supposed to exist in the solution of gold combined with muriatic acid. It may be prepared by mixing with a concentrated neutral solution of gold a quantity of pure potassa exactly sufficient for combining with the muriatic acid. A reddish-yellow coloured precipitate, the hydrous peroxide, subsides, which is rendered anhydrous by boiling, and assumes a brownish-black colour\*. The best method of forming it, according to M. Pelletier, is by digesting the muriate with pure magnesia, washing the precipitate with water, and removing the excess of magnesia by dilute nitric acid.

The peroxide of gold is yellow in the state of hydrate, and nearly black when pure, is insoluble in water, and is completely decomposed by solar light or a red heat. Muriatic acid dissolves it readily, yielding the common gold solution; but it forms no definite compound with any acid which contains oxygen. It may indeed be dissolved by the nitric and sulphuric acids; but the affinity is so slight that the oxide is precipitated by the addition of water. It combines, on the contrary, with alkaline bases, such as potassa and baryta, apparently forming regular salts, in which it acts the part of a weak acid. These circumstances have induced M. Pelletier to deny that the peroxide is a salifiable base, and to contend that the muriatic solution of gold is in reality a chloride of the metal. On this supposition he proposes the term *auric acid* for the peroxide of gold, and to its compounds with alkalies he gives the denomination of *aurates*.

The peroxide of gold is thrown down of a yellow colour by ammonia, and the precipitate is an aurate of that alkali. It is a highly detonating compound analogous to the fulminating silver described in the last section.

As chemists are but imperfectly acquainted with the number and composition of the oxides of gold, it is at present impossible to determine the atomic weight of this metal in a satisfactory manner. According to Berzelius†, 100 parts of gold unite with 12.077, according to Oberkampff‡ with 10.01, and according to Pelletier with 10.03 parts of oxygen to constitute the peroxide. M. Javal§ has more recently analyzed the oxide of gold, and finds that the proportion stated by Berzelius is very near the truth. If we adopt the numbers given

\* M. Pelletier in the An. de Ch. et de Ph. vol. xv.

† An. de Ch. vol. lxxxiii.

‡ Ibid. lxxx.

§ An. de Ch. et de Ph. vol. xvii.

by this chemist, and regard the peroxide as containing three atoms of oxygen, 200 will be the atomic weight of gold, and 224 the equivalent of its oxide. This view is supported by the result of the experiments of Dr Thomson. (First Principles, vol. i.)

*Chlorides of gold.*—On concentrating the solution of gold to a sufficient extent by evaporation, the perchloride may be obtained in red prismatic crystals, which become brown when brought to perfect dryness. It deliquesces on exposure to the air, and is dissolved readily by water without residue. At a temperature far below that of redness, it is converted, with evolution of two-thirds of its chlorine, into the yellow insoluble protochloride, from which the chlorine is entirely expelled by a red heat. This protochloride is converted, by being boiled in water, into the soluble perchloride and metallic gold.

The composition of the chlorides of gold was investigated by Berzelius and Pelletier; but the results of their analyses are so very discordant, that no satisfactory conclusion can be drawn from them.

The solution of gold is decomposed by substances which have a strong affinity for oxygen. On adding to it the protosulphate of iron dissolved in water, the iron is oxidized to a maximum, and a copious brown precipitate subsides, which is metallic gold in a state of very minute division.—This precipitate, when duly washed with dilute muriatic acid, in order to separate adhering iron, is gold in a state of perfect purity. A similar reduction is effected by most of the metals, and by sulphurous and phosphorous acids. When a piece of charcoal is immersed in the solution of gold, and exposed to the direct solar rays, its surface acquires a coating of metallic gold; and ribands may be gilded by moistening them with a dilute solution of gold, and exposing them to a current of hydrogen or phosphuretted hydrogen gas. When a strong aqueous solution of gold is shaken in a phial with an equal volume of pure ether, two fluids result, the lighter of which is an ethereal solution of gold. From this liquid flakes of metal are deposited on standing, especially by exposure to light, and substances moistened with it receive a coating of metallic gold\*.

When the protomuriate of tin is added to a dilute aqueous solution of gold, a purple coloured precipitate, called the *purple of Cassius*, is thrown down, which is the substance employed in painting on porcelain for giving a pink colour. It appears to be a compound of the protoxide of tin and the purple oxide of gold, in which the former is supposed to act as an acid.

*Sulphuret of gold.*—On transmitting a current of sulphuretted hydrogen gas through a solution of gold, a black precipitate is formed, which is a sulphuret. It is resolved by a red heat into gold and sulphur, and appears from the analysis of Oberkampf to be composed of 200 parts or one atom of gold, and 48 parts or three atoms of sulphur.

The compounds of gold with the other non-metallic bodies have been little examined.

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\* With respect to the revival of gold from its solutions, the reader may consult an Essay on Combustion, by Mrs Fulhame, and a paper by Count Rumford in the Philosophical Transactions for 1798.



## SECTION XXV.

## PLATINUM.

This valuable metal occurs only in the metallic state, associated or combined with various other metals, such as copper, iron, lead, gold, silver, palladium, rhodium, osmium, and iridium. It has hitherto been found chiefly in Brazil, Peru, and other parts of South America, in the form of rounded or flattened grains of a metallic lustre and white colour, mixed with sand and other alluvial depositions. Within these few months, however, M. Boussingault has discovered it in a syenitic rock in the province of Antioquia in North America, where it occurs in veins associated with gold. Rich mines of gold and platinum have also been recently discovered in the Uralian mountains. (*Edinburgh Journal of Science*, No. x.)

Pure platinum has a white colour very much like silver, but of inferior lustre. It is the heaviest of known metals, its density being about 21.5. Its malleability is considerable, though far less than that of gold and silver. It may be drawn into wires, the diameter of which does not exceed the 2000th part of an inch. It is a soft metal, and, like iron, admits of being welded at a high temperature. Dr Wollaston has observed that it is a less perfect conductor of caloric than most other metals.

Platinum undergoes no change from the combined agency of air and moisture; and it may be exposed to the strongest heat of a smith's forge without suffering either oxidation or fusion. On heating a small wire of it by means of galvanism or the oxy-hydrogen blowpipe, it is fused, and afterwards burns with the emission of sparks. The late Mr Smithson Tennant showed that it is oxidized when ignited with nitre; (*Philos. Trans.* for 1797;) and a similar effect is occasioned by pure potassa and lithia.

Platinum is not attacked by any of the pure acids. Its only solvents are chlorine and nitro-muriatic acid, which act upon it with greater difficulty than on gold. The resulting orange-red coloured liquid, from which the excess of acid should be expelled by cautious evaporation, may be regarded as containing either the chloride of platinum, or the muriate of its oxide.

*Oxides of platinum.*—According to Berzelius there are two oxides of platinum, the oxygen of which is in the ratio of 1 to 2\*. The protoxide is prepared by the action of potassa on the protochloride of platinum. It is of a black colour, is reduced by a red heat, and is composed of 96.5 parts of platinum, and 8 parts of oxygen. Now, Dr Thomson infers from his researches, that 96 is the atomic weight of platinum, from which it is probable that the two oxides of Berzelius are thus constituted:—

	Platinum.	Oxygen.
Protoxide	96	8
Peroxide	96	16

The peroxide has not hitherto been obtained in a perfectly pure state. Berzelius supposes it to exist in the muriate of platinum com-

\* *Ann. de Chem.* vol. xxxviii.

bined with muriatic acid ; and Dr Thomson states that it is contained in the sulphate of platinum.

Another oxide was described by Mr E. Davy in the Philosophical Transactions for 1820. It is of a gray colour, and is prepared by heating fulminating platinum with nitrous acid. It appears from his analysis to be composed of 96 parts or one atom of platinum, and 12 parts or an atom and a half of oxygen. Mr Cooper has likewise described an oxide of platinum ; but its existence as a definite compound distinct from those above described has not, I conceive, been satisfactorily demonstrated.

*Chlorides of Platinum.*—The perchloride is procured by evaporating the muriate of platinum to dryness at a gentle heat. It is deliquescent, and is soluble both in water, alcohol, and ether. The ethereal solution is decomposed by the agency of light, metallic platinum being deposited. It is probable from the analysis of the double chloride of potassium and platinum by Dr Thomson and Berzelius, that the perchloride of platinum is composed of 96 parts or one atom of metal to 72 parts or two atoms of chlorine ; but this inference requires confirmation.

When the perchloride is strongly heated, it parts with some of its chlorine, and is converted into a protochloride, which is resolved by a red heat into platinum and chlorine.

Platinum is distinguished from all other substances by the following circumstances. When pure potassa or a salt of potassa is added to a concentrated solution of platinum, a yellow crystalline precipitate subsides, which is very sparingly soluble in water. When heated to full redness chlorine gas is disengaged, and the residue consists of metallic platinum and the chloride of potassium. According to the analysis of Thomson it is composed of

Bichloride of Platinum	.	168 or one atom.
Chloride of Potassium	.	76 or one atom.

Ammonia or its salts produce a similar precipitate, which is composed according to Dr Thomson of

Bichloride of Platinum	.	168 or one atom.
Muriate of Ammonia	.	54 or one atom.

When this compound, which is generally called the *muriate of platinum* and *ammonia*, is heated to redness, chlorine and muriate of ammonia are evolved, and pure platinum remains in the form of a delicate spongy mass, the power of which in kindling an explosive mixture of oxygen and hydrogen gases has already been mentioned. (Page 116.) This salt affords an easy method of procuring platinum in a metallic state and of separating it from other metals.

Soda forms with muriate of platinum a double salt, which is soluble in water and alcohol, and crystallizes in flattened, oblique, four-sided prisms of an orange-red colour. According to Dr Thomson it is a compound of one atom of the bichloride of platinum, one atom of the chloride of sodium, and eight atoms of water.

*Sulphuret of Platinum.*—When sulphuretted hydrogen gas is transmitted through a solution of the muriate of platinum, a black precipitate is thrown down, which Vauquelin regards as a hydrosulphuret of the oxide of platinum. It absorbs oxygen from the air while in a moist state, give rise to the formation of sulphuric acid. Its composition has not been determined with accuracy.

A black sulphuret of platinum was procured by Mr E. Davy by heating the metal with sulphur, and Vauquelin obtained a similar compound by igniting the yellow muriate of platinum and ammonia with twice its weight of sulphur. According to the analysis of these chemists, it contains about 16 per cent. of sulphur.

The hydrosulphuret of platinum is converted by the action of nitric acid into a sulphate which possesses remarkable properties. On boiling it in strong alcohol, a black powder is precipitated, which consists, according to Mr E. Davy, of 96 per cent. of platinum, together with a little oxygen, nitrous acid, and carbon, the last of which is supposed to be accidental. When this powder is placed on bibulous paper moistened with alcohol, a strong action accompanied with a hissing noise ensues, and the powder becomes red-hot, and continues so until the alcohol is consumed. The substance which remains is pure platinum.

Fulminating platinum may be prepared by the action of ammonia in slight excess on a solution of the sulphate of platinum. (E. Davy.) It is analogous to the detonating compounds which ammonia forms with the oxides of gold and silver.

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## SECTION XXVI.

### *PALLADIUM. RHODIUM. OSMIUM. IRIDIUM.*

The four metals to be described in this section are all contained in the ore of platinum, and have hitherto been procured in very small quantity. When the ore is digested in nitro-muriatic acid, the platinum, together with palladium, rhodium, iron, copper, and lead, is dissolved; while a black powder is left consisting of osmium and iridium.

#### *Palladium.*

This metal was discovered in 1803 by Dr Wollaston\*. On adding cyanuret of mercury dissolved in water to a neutral solution of the ore of platinum, either before or after the separation of that metal by muriate of ammonia, a yellowish-white flocculent precipitate is gradually deposited, which is a cyanuret of palladium. When this compound is heated to redness, the cyanogen is expelled, and pure palladium remains.

Palladium resembles platinum in colour and lustre. It is both malleable and ductile, and considerably harder than platinum. Its specific gravity varies from 11.3 to 11.8. (Wollaston.) In fusibility it is intermediate between gold and platinum, and it is dissipated in sparks when intensely heated by the oxyhydrogen blow-pipe.

Palladium is oxidized and dissolved by nitric acid, and even the sulphuric and muriatic acids act upon it by the aid of heat; but its proper solvent is the nitro-muriatic acid. Its oxide forms beautiful red-coloured salts, from which metallic palladium is precipitated by the protosulphate of iron and by all the metals described in the foregoing sections, excepting silver, gold, and platinum.

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\* Philosophical Transactions for 1804 and 1805.

The oxide of palladium is precipitated by pure potassa, as an orange-coloured hydrate, which becomes black when dried, and is decomposed by a red heat. It consists, according to Berzelius, of nearly 56 parts of palladium and 8 parts of oxygen; so that 56 is most probably the atomic weight of the metal itself, and 64 the equivalent of its oxide.

### Rhodium.

This metal was discovered by Dr Wollaston at the time he was occupied with the discovery of palladium. On immersing a thin plate of clean iron into the solution from which palladium and the greater part of the platinum have been precipitated, the rhodium, together with small quantities of platinum, copper, and lead, is thrown down in the metallic state; and on digesting the precipitate in dilute nitric acid, the two last metals are removed. The rhodium and platinum are then dissolved by means of nitro-muriatic acid, and the solution, after being mixed with some muriate of soda, is evaporated to dryness. Two double salts result, the muriate of platinum and soda, and the muriate of rhodium and soda, the former of which is soluble and the latter insoluble in alcohol, and may therefore be separated from one another by that menstruum. The salt of rhodium is then dissolved in water, and the pure rhodium precipitated by insertion of a rod of zinc.

Rhodium, thus procured, is in the form of a black powder, which requires the strongest heat that can be produced in a wind furnace for fusion, and when fused has a white colour and metallic lustre. It is brittle, and its specific gravity is about 11. It is not attacked by any of the acids when in its pure state; but if alloyed with other metals, such as copper or lead, it is oxidized and dissolved by the nitro-muriatic acid, a circumstance which accounts for its presence in the solution of crude platinum. It is oxidized also by being ignited with nitre. Most of its salts are either red or yellow, and the muriate is of a rose-red colour, from which it has received the name of *rhodium*\*.

The number deduced by Dr Thomson as the atomic weight of rhodium is 44; and its oxides, according to the same chemist, are thus constituted:—

	<i>Rhodium.</i>	<i>Oxygen.</i>
Protoxide .	44	8
Peroxide .	44	16

The protoxide is black, and the peroxide, which is the base of the salts of rhodium, is of a yellow colour. Berzelius, whose results do not accord with those of Dr Thomson, has described a brown oxide; but it is as yet undetermined whether it is a distinct oxide or a mixture of the two others.

### Iridium and Osmium.

These metals were discovered by the late Mr Tennant in the year

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\* From *ῥόδον* a rose.

1803\*, and the discovery of iridium was made about the same time by M. Descotils in France. The black powder mentioned at the beginning of this section is a compound of iridium and osmium, an alloy which Dr Wollaston has detected in the form of flat white grains among fragments of crude platinum. From this alloy, which is quite insoluble in nitro-muriatic acid, Mr Tennant prepared iridium and osmium in the following manner. The black powder mixed with soda was heated to redness in a silver crucible, and the residue, after removing the alkali by means of water, was digested in muriatic acid. In this way two solutions, one alkaline and the other acid, were procured, the former of a deep orange-colour, containing the oxide of osmium united with soda, and the latter, the muriate of iridium. From the refractory nature of the alloy, it is necessary to ignite with successive portions of soda before the whole of any given quantity of the black powder is oxidized.

*Osmium*.—On neutralizing the alkaline liquid just described, and heating it in a retort, the oxide of osmium, which is both volatile and soluble in water, passes over into the recipient, and is there dissolved in the fluid that accompanies it. The aqueous solution is colourless, and emits a pungent peculiar odour, somewhat like that of chlorine, a property which suggested the name of *osmium*†. The oxide of osmium has not been procured free from water, nor has its composition been determined. The infusion of gall-nuts is a delicate test of its presence, striking a purple colour which afterwards acquires a deep blue tint.

The oxide of osmium is precipitated in the metallic state by nearly all the metals, excepting gold and platinum. On agitating it with mercury an amalgam is formed, which, when heated in close vessels, yields pure osmium, capable of supporting a white heat without being volatilized or fused. If ignited in open vessels, it is oxidized and is then dissipated in vapour. After exposure to heat it resists the action of all the acids.

*Iridium*. The solution of the oxide of iridium in muriatic acid, when first prepared, is of a blue colour; but it afterwards becomes of an olive-green hue, and subsequently acquires a deep red tint. This diversity of colour, which gave origin to the name of iridium, is attributed to the metal passing through different stages of oxidation, an opinion which is probable, though by no means established. Chemists, indeed, are as yet ignorant both of the number and composition of the oxides of iridium.

The muriate of iridium, when deprived of its excess of acid by heat, may be procured in crystals of a deep brown colour by evaporation. This salt is characterized by forming with water a red solution, which is rendered colourless by the pure alkalies or alkaline earths, by sulphuretted hydrogen, infusion of gall-nuts, or by the ferrocyanate of potassa. It is decomposed by nearly all the metals excepting gold and platinum, the iridium being thrown down in the metallic state. Iridium may likewise be procured from the muriate by exposing that salt to a red heat.

Iridium is the most infusible metal known; but Mr Children, by means of his large galvanic battery, succeeded in fusing it into a glo-

\* Philosophical Transactions for 1804.

† From *ὀσμή* odour.



bule of a brilliant metallic lustre and white colour. Its specific gravity in this state is 18.68. It is attacked with great difficulty by nitromuriatic acid; but is oxidized when heated with nitre.

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## SECTION XXVII.

### ON METALLIC COMBINATIONS.

Having completed the history of the individual metals, and of the compounds resulting from their union with the simple non-metallic bodies, I shall treat briefly in the present section of the combinations of the metals with one another. These compounds are called *alloys*; and to those alloys of which mercury is a constituent, the term *amalgam* is applied. It is probable that each metal is capable of uniting in one or more proportions with every other metal, and on this supposition the number of alloys would be exceedingly numerous. This department of chemistry, however, owing to its having been cultivated with less zeal than most other branches of the science, is as yet limited, and our knowledge concerning it imperfect. On this account I shall mention those alloys only to which some particular interest is attached.

Metals do not combine with one another in their solid state, owing to the influence of chemical affinity being counteracted by the force of cohesion. It is necessary to liquefy at least one of them, in which case they always unite, provided their mutual attraction is energetic. Thus brass is formed when pieces of copper are put into melted zinc; and gold unites with mercury at common temperatures by mere contact.

Metals appear to unite with one another in every proportion, precisely in the same manner as sulphuric acid and water. Thus there is no limit to the number of alloys of gold and copper. It is certain, however, that metals have a tendency to combine in definite proportion; for several atomic compounds of this kind occur native. The crystallized amalgam of silver, for example, is composed, according to the analysis of Klaproth, of 64 parts of mercury and 36 of silver, numbers which are so nearly in the ratio of 200 to 110, that there can be no doubt of the amalgam containing one atom of each of its elements. It is indeed possible that the variety of proportion is rather apparent than real, arising from the mixture of a few definite compounds with one another, or with uncombined metal, an opinion not only suggested by the mode in which alloys are prepared, but in some measure supported by observation. Thus on adding successive small quantities of silver with mercury, a great variety of fluid amalgams are apparently produced; but, in reality, the chief, if not the sole compound, is a solid amalgam, which is merely diffused throughout the fluid mass, and may be separated by pressing the liquid mercury through a piece of thick leather.

Alloys are analogous to metals in their chief physical properties. They are opaque, possess the metallic lustre, and are good conductors of electricity and caloric. They often differ materially in some respects from the elements of which they consist. The colour of an

alloy is sometimes different from that of its constituents, of which brass is a remarkable example. The hardness of a metal is in general increased by being alloyed, and for this reason its elasticity and sonorousness are frequently improved. The malleability and ductility of metals, on the contrary, are usually impaired by combination. Alloys formed of two brittle metals are always brittle; and an alloy composed of a ductile and a brittle metal is generally brittle, especially if the latter predominate. An alloy of two ductile metals is sometimes brittle.

The density of alloys is sometimes less, sometimes greater, than the mean density of the metals of which it is composed.

The fusibility of metals is greatly increased by being alloyed. Thus, pure platinum, which cannot be completely fused in the most intense heat of a wind furnace, forms a very fusible alloy with arsenic.

The tendency of metals to unite with oxygen is considerably augmented by being alloyed. This effect is particularly conspicuous when dense metals are liquefied by combination with quicksilver, and is manifestly owing to the loss of their cohesive power. Lead and tin, for instance, when united with mercury, are soon oxidized by exposure to the atmosphere; and even gold and silver combine with oxygen, when the amalgams of those metals are agitated with air. The oxidability of one metal in an alloy appears in some instances to be increased in consequence of a galvanic action. Thus Mr Faraday observed, that an alloy of steel with 100th of its weight of platinum was dissolved with effervescence in dilute sulphuric acid, which was so weak that it scarcely acted on common steel;—an effect which he ascribes to the steel in the alloy being rendered positive by the presence of the platinum.

### *Amalgams.*

Quicksilver unites with potassium when agitated in a glass tube with that metal, forming a solid amalgam. When the amalgam is put into water, the potassium is gradually oxidized, hydrogen gas is disengaged, and the mercury resumes its liquid form. A similar compound may be obtained with sodium. These amalgams may also be procured by placing the negative wire in contact with a globule of mercury during the process of decomposing potassa and soda by galvanism. (Page 242.)

A solid amalgam of tin is employed in making looking-glasses; and an amalgam made of one part of lead, one of tin, two of bismuth, and four parts of mercury, is used for silvering the inside of hollow glass globes. This amalgam is solid at common temperatures; but is fused by a slight degree of heat.

The amalgam of zinc and tin, used for promoting the action of the electrical machine, is made by fusing one part of zinc with one of tin, and then agitating the liquid mass with two parts of mercury placed in a wooden box. Mercury evinces little disposition to unite with iron, and, on this account, it is usually preserved in iron bottles.

The amalgam of silver, as already mentioned, is a mineral production. The process of separating silver from its ores by amalgamation, practised on a large scale at Freyberg in Germany, is founded on the affinity of mercury for silver. On exposing the amalgam to heat, the quicksilver is volatilized, and pure silver remains.

Gold unites with remarkable facility with mercury, forming a white-coloured compound. An amalgam composed of one part of gold to

eight of mercury is employed in gilding brass. The brass, after being rubbed with the nitrate of mercury in order to give it a thin film of quicksilver, is covered with the amalgam of gold, and then exposed to heat for the purpose of expelling the mercury.

### *Alloys of Arsenic.*

Arsenic has a tendency to render the metals, with which it is alloyed, both brittle and fusible. It has the property of destroying the colour of gold and copper. An alloy of copper, with a tenth part of arsenic, is so very similar in appearance to silver, that it has been substituted for it. The whiteness of this alloy affords a rough mode of testing for arsenic; for if arsenious acid and charcoal be heated between two plates of copper, a white stain afterwards appears upon its surface, owing to the formation of an arseniuret of copper.

The presence of arsenic in iron has a very pernicious effect; for even though in a small proportion, it renders the iron brittle, especially when heated.

The alloy of tin and arsenic is employed for forming arseniuretted hydrogen gas by the action of muriatic acid. The tin of commerce sometimes contains a minute quantity of this alloy.

An alloy of platinum with ten parts of arsenic is fusible at a heat a little above redness, and may therefore be cast in moulds. On exposing the alloy to a gradually increasing temperature in open vessels, the arsenic is oxidized and expelled, and the platinum recovers its purity and infusibility.

### *Alloys of Tin, Lead, Antimony, and Bismuth.*

Tin and lead unite readily when fused together. Equal parts of these metals constitute an alloy which is more fusible than either separately, and is the common solder of the glaziers.

Tin alloyed with small quantities of antimony, copper, and bismuth, forms the best kind of pewter. Inferior sorts contain a large proportion of lead.

Tin, lead, and bismuth, form an alloy which is fused by a temperature below  $212^{\circ}$  Fahr. The best proportion, according to M. D'Arcet, is eight parts of bismuth, five of lead, and three of tin.

An alloy of three parts of lead to one of antimony constitutes the substance of which types for printing are made.

### *Alloys of Copper.*

Copper forms with tin several valuable alloys, which are characterized by their sonorousness. Bronze is an alloy of copper with about eight or ten per cent. of tin, together with small quantities of other metals which are not essential to the compound. Cannons are cast with an alloy of a similar kind.

The best bell-metal is composed of 80 parts of zinc and 20 of tin;—the Indian gong, celebrated for the richness of its tones, contains copper and tin in this proportion. A specimen of English bell-metal was found by Dr Thomson to consist of 80 parts of copper, 10.1 of tin, 5.6 of zinc, and 4.3 of lead. Lead and antimony, though in small quantity, have a remarkable effect in diminishing the elasticity and sonorousness of the compound. The *speculum-metal*, with which mir-

rors for telescopes are made, consists of about two parts of copper and one of tin. The whiteness of the alloy is improved by the addition of a little arsenic.

Copper and zinc unite in several proportions, forming alloys of great importance in the arts. The best brass consists of four parts of copper to one of zinc; and when the latter is in a greater proportion, compounds are generated which are called *Tombac*, *Dutch-gold*, and *Pinchbeck*. The *white copper* of the Chinese is composed, according to the analysis of Dr Fyfe, of 40.4 parts of copper, 25.4 of zinc, 31.6 of nickel, and 2.6 of iron.

The art of tinning copper consists in covering that metal with a thin layer of tin, in order to protect its surface from rusting. For this purpose, pieces of tin are placed upon a well-polished sheet of copper, which is heated sufficiently for fusing the tin. As soon as the tin liquefies, it is rubbed over the whole sheet of copper, and, if the process is skilfully conducted, adheres uniformly to its surface. The oxidation of the tin, a circumstance which would entirely prevent the success of the operation, is avoided by employing fragments of resin or muriate of ammonia, and regulating the temperature with great care. The two metals do not actually combine with one another; but the adhesion is certainly owing to their mutual affinity.—Iron, which has a weaker attraction than copper for tin, is tinned with more difficulty than that metal.

### *Alloys of Steel.*

Messrs Stodart and Faraday have succeeded in making some very important alloys of steel with other metals. (Philos. Trans. for 1822.) Their experiments induced them to believe, that the celebrated Indian steel called *wootz*, is an alloy of steel with small quantities of silicium and aluminum; and they succeeded in preparing a similar compound, possessed of all the properties of *wootz*. They ascertained that silver combines with steel, forming an alloy which, although it contains only 1-500th of its weight of silver, is superior to *wootz* or the best cast steel in hardness. The alloy of steel with 100th part of platinum, though less hard than that with silver, possesses a greater degree of toughness, and is therefore highly valuable when tenacity as well as hardness is required. The alloy of steel with rhodium even exceeds the two former in hardness. The compound of steel with palladium, and of steel with iridium and osmium, is likewise exceedingly hard; but these alloys cannot be applied to useful purposes, owing to the rarity of the metals of which they are composed.

### *Alloys of Silver.*

Silver is capable of uniting with most other metals, and suffers greatly in malleability and ductility by their presence. It may contain a large quantity of copper without losing its white colour. The standard silver for coinage contains about 1-13th part of copper, which increases its hardness, and thus renders it more fit for coins and many other purposes.

### *Alloys of Gold.*

The presence of other metals in gold has a remarkable effect in im-

pairing its malleability and ductility. The metals which possess this property in the greatest degree are bismuth, lead, antimony, and arsenic. Thus, when gold is alloyed with 1-1920th part of its weight of lead, its malleability is surprisingly diminished. A very small proportion of copper has an influence over the colour of gold, communicating to it a red tint, which becomes deeper as the quantity of copper increases. Pure gold, being too soft for coinage and many purposes in the arts, is always alloyed either with copper or an alloy of copper and silver, which increases the hardness of the gold without materially affecting its colour or tenacity. Gold coins contain about 1-12th of copper.



## SALTS.

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### GENERAL REMARKS ON SALTS.

IN the preceding pages I have been chiefly occupied with the description either of elementary principles, or of compounds immediately resulting from their union. The class of bodies which I am now to describe is of a different nature, being exclusively compounds derived from the combination of other compound bodies.

By the term *salt* chemists mean a definite compound of an acid, and of an alkaline or salifiable base, both of which are in every case composed of at least two simple substances. Sulphate of potassa, for instance, is a salt, the acid of which consists of oxygen and sulphur, and the base of oxygen and potassium. A different view may indeed be formed of the nature of a salt. Thus, to employ the example already adduced, sulphate of potassa contains sulphur, oxygen, and potassium; and it may be thought that these three elements do not exist in the salt as sulphuric acid and potassa, but are combined directly and indiscriminately with one another. But such an opinion is gratuitous and untenable. Sulphate of potassa is said to contain sulphuric acid and potassa, because, in the first place, it is formed by the direct mixture of these two substances; secondly, because the acid and the alkali, after combination, may be separated and again procured in their original state by the agency of galvanism; and, thirdly, because no known affinity is in operation by which the tendency of potassium to constitute potassa with oxygen, or of sulphur to form sulphuric acid with the same element, may be counteracted. It is probable, indeed, that all compounds consisting of three or more elementary principles, are composed of binary compounds united with one another.

In studying the salts, it is important to set out with correct ideas concerning the nature of an acid and of an alkaline base, and I shall therefore make a few preliminary remarks concerning the nature and characteristic properties of these two classes of compounds.

An acid is commonly regarded as a substance which has a sour taste, reddens litmus paper, and neutralizes alkalies. But these properties, though very conspicuous in all the powerful acids, are not altogether general, and therefore cannot serve the purpose of a definition. Thus insoluble acids, owing to their insolubility, do not taste sour, nor redden litmus paper; and some bodies, such as carbonic acid and sulphuretted hydrogen, the title of which to be placed among the acids cannot be called in question, are unable to destroy the alkaline reaction of potassa. The most correct definition of an acid with which I am acquainted is the following:—an acid is a compound, which is capable of uniting in definite proportion with alkaline bases, and which, when

liquid or in a state of solution, has either a sour taste, or reddens litmus paper.

Most of the acids contain oxygen as one of their elements, a circumstance which induced Lavoisier to suppose that oxygen possesses some specific power of causing acidity, and for this reason he regarded it as the *acidifying principle*. The acquisition of new facts, however, has shown the fallacy of his opinion. Acids may and do exist which contain no trace of oxygen, nor does its presence necessarily give rise to acidity. The compounds of oxygen are frequently alkaline instead of acid; and in many instances they are neither acid nor alkaline. No substance contains a larger proportional quantity of oxygen than water, and yet this fluid does not possess the slightest degree of acidity. The progress of science, indeed, seems to justify the opinion that there is no body to which the term acidifying principle is strictly applicable. The acidity of any substance cannot be referred to one of its elements rather than the other; but is a new property peculiar to the compound, and to which each of its constituents equally contributes.

An alkali is characterized by a peculiar pungent taste, by its alkaline reaction on vegetable colours, and by neutralizing acids. There are many salifiable bases, however, which do not possess these characters. Thus pure magnesia, though it is a strong alkaline base and forms neutral salts with acids, is insipid, and barely produces an appreciable effect on yellow turmeric paper,—an inaction obviously owing to its insolubility. Some compounds neutralize the properties of acids in an imperfect manner, although they form perfect salts. For these reasons it is desirable to define precisely what is meant by a salifiable base, and the following definition appears to me to answer the purpose. Every compound may be regarded as an alkaline or salifiable base, which forms definite compounds with acids, and which, when liquid or in a state of solution, has an alkaline reaction. All alkaline bases, with the exception of ammonia and the vegetable alkalies, are metallic oxides.

I have already explained the nomenclature of the salts. (Page 77.) The insufficiency of the division into *neutral*, *super*, and *sub-salts* will be made apparent by the following remarks. In the first place, some alkaline bases form more than one super-salt, in which case two or more different salts would be included under the same name. Secondly, some salts have an acid reaction, and might therefore be denominated super-salts, although they do not contain an excess of acid. The nitrate of lead, for instance, has the property of reddening litmus paper; whereas it consists of one atom of the oxide of lead and one atom of nitric acid, and therefore in composition is precisely analogous to the nitrate of potassa, which is a neutral salt. This fact was noticed some years ago by Berzelius, who accounted for the circumstance in the following manner. The colour of litmus is naturally red, and it is only rendered blue by the colouring matter combining with an alkali. If an acid be added to the blue compound, the colouring matter is deprived of its alkali, and thus, being set free, resumes its red tint. Now on bringing litmus paper in contact with a salt, the acid and base of which have a weak attraction for each other, it is possible that the alkali contained in the litmus paper may have a stronger affinity for the acid of the salt than the base has with which it was combined, and in that case, the alkali of the litmus being neutralized, its red colour would necessarily be restored. It is hence

apparent that a salt may have an acid reaction without having an excess of acid.

As every acid, with few exceptions, is capable of uniting with every alkaline base, and frequently in two or more proportions, it is manifest that the salts must constitute a very numerous class of bodies. It is necessary, on this account, to facilitate the study of them as much as possible by classification. They may be conveniently arranged by placing together those salts which contain either the same salifiable base or the same acid. It is not very material which principle of arrangement is adopted; but I give the preference to the latter, because, in describing the individual oxides, I have already mentioned the characteristic features of their salts, and have thus anticipated the chief advantage that arises from the former mode of classification. I shall therefore divide the salts into groups, placing together those saline combinations which consist of the same acid, united with different salifiable bases. The salts of each group, in consequence of containing the same acid, possess certain characters in common by which they may all be distinguished; and, indeed, the description of many salts, to which no particular interest is attached, is sufficiently comprehended in that of its group, and may therefore be omitted.

Nearly all salts are solid, and most of them assume crystalline forms when their solutions are spontaneously evaporated.

The colour of salts is very variable. Those that are composed of a colourless base and acid are always colourless. There is no necessary connexion between the colour of an oxide or an acid and that of its salts. A salt, though formed of a coloured oxide or acid, may be colourless; and if it is coloured, the tint may differ from that of both its constituents.

All soluble salts are more or less sapid, while those that are insoluble in water are insipid. Few salts are possessed of odour: the only one which is remarkable for this property is the carbonate of ammonia.

Salts differ remarkably in their affinity for water. Thus some salts, such as the nitrates of lime and magnesia, are *deliquescent*, that is, attract moisture from the air and become liquid. Others, which have a less powerful attraction for water, undergo no change when the air is dry, but become moist in a humid atmosphere; and others may be exposed without change to an atmosphere loaded with watery vapour.

Salts differ likewise in the degree of solubility in water. Some dissolve in less than their weight of water; while others require several hundred times their weight of this liquid for solution, and others are quite insoluble. This difference depends on two circumstances, namely, on the degree of their affinity for water, and on their cohesion; their solubility being in direct ratio with the first, and in inverse ratio with the second. One salt may have a greater affinity for water than another, and yet be less soluble; an effect which may be produced by the cohesive power of the salt, which has the stronger attraction for water, being greater than that of the salt which has a less powerful affinity for that liquid. The method proposed by Gay-Lussac for estimating the relative degrees of affinity of salts for water, (*An. de Ch.* lxxxii.) is by dissolving equal quantities of salts in equal quantities of water, and applying heat to the solutions. That salt which has the greatest affinity for the menstruum will retain it with most force, and will therefore require the highest temperature for boiling.

Salts which are soluble in water crystallize more or less regularly when their solutions are evaporated. If the evaporation is rendered,

rapid by heat, the salt is usually deposited in a fused crystalline mass; but if it take place slowly, regular crystals are formed. The best mode of conducting the process, is to dissolve a salt in hot water, and, when it has become quite cold, to pour the saturated solution into an evaporating basin, which is to be set aside for several days or weeks without being moved. As the water evaporates, the salt assumes the solid form; and the slower the evaporation, the more regular are the crystals. Some salts which are much more soluble in hot than in cold water, crystallize with considerable regularity when a boiling saturated solution is slowly cooled. The form which salts assume in crystallizing is constant under the same circumstances, and constitutes an excellent character by which they may be distinguished from one another.

Many salts during the act of crystallizing unite chemically with a definite portion of water, which forms an essential part of the crystal, and is termed the *water of crystallization*. The quantity of combined water is very variable in different saline bodies, but is uniform in the same salt. A salt may contain more than half its weight of water, and yet be quite dry. On exposing a salt of this kind to heat, it is dissolved, if soluble, in its own water of crystallization, undergoing what is termed the *watery fusion*. By a strong heat, the whole of the water is expelled; for no salt can retain its water of crystallization when heated to redness. Some salts, such as the sulphate and phosphate of soda, lose a portion of their water, and crumble down into a white powder, by mere exposure to the air, a change which is called *efflorescence*.

Salts, in crystallizing, frequently inclose mechanically within their texture particles of water, by the expansion of which, when heated, the salt is burst with a crackling noise into smaller fragments. This phenomenon is known by the name of *decrepitation*. Berzelius has correctly remarked that those crystals decrepitate most powerfully, such as the nitrates of baryta and of lead, which contain no water of crystallization.

The atmospheric pressure is said to have considerable influence on the crystallization of salts. If, for example, a concentrated solution, composed of about three parts of sulphate of soda in crystals to two of water, is made to boil briskly, and the flask which contains it is then tightly corked, while its upper part is full of vapour, the solution will cool down to the temperature of the air without crystallizing, and may in that state be preserved for months without change. Before removal of the cork, the liquid may often be briskly agitated without losing its fluidity; but on re-admitting the air, crystallization commonly commences, and the whole becomes solid in the course of a few seconds. The admission of the air sometimes, indeed, fails in causing the effect; but it may be produced with certainty by agitation or the introduction of a solid body. The theory of this phenomenon is not very apparent. Gay-Lussac has shown that it does not depend on atmospheric pressure; (*An. de Ch.* vol. lxxxvii.) for he finds that the solution may be cooled in open vessels without becoming solid, provided its surface be covered with a film of oil; and I have frequently succeeded in the same experiment without the use of oil, by causing the air of the flask to communicate with the atmosphere by means of a moderately narrow tube.

The same quantity of water may hold several different salts in solution, provided they do not mutually decompose each other. The sol-

vent power of water with respect to one salt is, indeed, sometimes increased by the presence of another, owing to combination taking place between the two salts.

Most salts produce cold during the act of dissolving in water, especially when they are dissolved rapidly and in large quantity. The greatest reduction of temperature is occasioned by those which contain water of crystallization.

All salts are decomposed by Voltaic electricity, provided they are either moistened or in solution. The acid appears at the positive pole of the battery, and the oxide at its opposite extremity; or, if the oxide is of easy reduction, the metal itself goes over to the negative side, and its oxygen accompanies the acid to the positive wire.

The composition of salts is subject to the laws of chemical union, and, indeed, the study of these compounds by Wenzel, Richter, and Berzelius, together with the facts ascertained by Dr Wollaston and Dr Thomson, tended materially to establish the doctrine of definite proportion. All salifiable bases, consisting of one atom of a metal and one atom of oxygen, are converted into neutral salts, that is, into salts without excess either of acid or of base, by uniting with one atom of an acid. (Page 94.) When a metal forms two salifiable bases with oxygen, the peroxide manifests a tendency to unite with more acid than the protoxide, and Gay-Lussac has demonstrated the existence of the following law:—*that the quantity of acid which the oxides of the same metal require for saturation, is in the same ratio as the quantity of oxygen contained in their oxides.* (Mémoires D'Arcueil, vol. ii.) Thus, while the protosulphate of iron contains one atom of each of its elements, the soluble per-sulphate is composed of one atom of the peroxide of iron, and one atom and a half of sulphuric acid. In like manner, the peroxides of mercury and copper are disposed to unite with two atoms or twice as much acid as would form a neutral salt with the protoxides of those metals. Hence, when a peroxide unites with one atom of an acid, the product is commonly a sub-salt.

The combination of salts with one another gave rise to compounds which were formerly called *triple* salts; but as the term *double* salt, proposed by Berzelius, gives a more correct idea of their nature and constitution, I shall always employ it by preference.\* These salts may be composed either of one acid and two bases, or of two acids and one base, and most probably of two different acids and two different bases. Nearly all the double salts hitherto examined, consist of the same acid and two different bases.

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## SECTION I.

**SULPHATES.—SULPHITES.—HYPOSULPHATES.—  
HYPOSULPHITES.**

### *Sulphates.*

The salts of sulphuric acid in solution may be detected by the muriate of baryta. A white precipitate, the sulphate of baryta, invariably subsides, which is insoluble in all the acids and alkalies, a character



by which the presence of sulphuric acid, whether free or combined, may always be recognised. An insoluble sulphate, such as the sulphate of baryta or strontia, may be detected by mixing it, in fine powder, with three times its weight of the carbonate of potassa or soda, and exposing the mixture in a platinum crucible for half an hour to a red heat. Double decomposition ensues; and on digesting the residue in water, filtering the solution, neutralizing the free alkali by pure muriatic, nitric, or acetic acid, and adding the muriate of baryta, the insoluble sulphate of that base is precipitated.

Several of the sulphates exist in nature, but the only ones which are abundant are the sulphates of lime and baryta. All of them may be formed by the action of sulphuric acid on the metals themselves, on the metallic oxides or their carbonates, or by way of double decomposition.

The solubility of the sulphates is very variable. There are six only which may be regarded as really insoluble; namely, the sulphates of baryta, tin, antimony, bismuth, lead, and mercury. The sparingly soluble sulphates are those of strontia, lime, zirconia, yttria, cerium, and silver. All the others are soluble in water.

All the sulphates, those of potassa, soda, lithia, baryta, strontia, and lime excepted, are decomposed in a white heat. One part of the sulphuric acid of the decomposed sulphate escapes unchanged, and another portion is resolved into sulphurous acid and oxygen. Those which are easily decomposed by heat, such as the sulphate of iron, yield the largest quantity of undecomposed sulphuric acid.

When a sulphate, mixed with carbonaceous matter, is ignited, the oxygen both of the acid and of the oxide unites with carbon, carbonic acid is disengaged, and a metallic sulphuret remains. A similar change is produced by hydrogen gas at a red heat, with formation of water, and frequently of some sulphuretted hydrogen. In some instances the hydrogen entirely deprives the metal of its sulphur.

The composition of the sulphates, so far as they are subject to general laws, has already been described. (Page 106.)

*Sulphate of Potassa.*—This salt is easily prepared artificially by neutralizing the carbonate of potassa with sulphuric acid, and it is procured abundantly as a product of the operation for preparing nitric acid. (Page 138.) Its taste is saline and bitter. It crystallizes in six-sided prisms, bounded by pyramids with six sides. The crystals contain no water of crystallization, and suffer no change by exposure to the air. They decrepitate when heated, and enter into fusion at a red heat. They require 16 times their weight of water at 60° F. and five of boiling water for solution.

The sulphate of potassa is composed of 40 parts or one atom of sulphuric acid, to 48 parts or one atom of potassa.

The bisulphate of potassa, which contains twice as much acid as the foregoing salt, is easily formed by digesting 88 parts, or one atom of the neutral sulphate, with water containing about 50 parts of concentrated sulphuric acid, and evaporating the solution. It has a strong sour taste, and reddens litmus paper. It is much more soluble than the neutral sulphate, requiring for solution only twice its weight of water at 60° and less than an equal weight at 212° F. It is resolved by heat into sulphuric acid and the neutral sulphate.

*Sulphate of Soda.*—The sulphate of soda, commonly called *Glauber's salt*, is occasionally met with on the surface of the earth, and is frequently contained in mineral springs. It may be made by the direct

action of sulphuric acid on the carbonate of soda ; and it is procured in large quantity as a residue in the processes for forming muriatic acid and chlorine. (Pages 164 and 168.)

The sulphate of soda has a cooling, saline, and bitter taste. It forms four and six-sided prismatic crystals, which effloresce rapidly when exposed to the air; and, according to Berzelius, are composed of 72 parts or one atom of the neutral sulphate, and 90 parts or ten atoms of water. The crystals readily undergo the watery fusion when heated, and dissolve in three times their weight of water at 60° Fahr.

The *bisulphate* of soda may be formed in the same manner as the analogous salt of potassa.

*Sulphate of Lithia*.—This salt is very soluble in water, fuses by heat more readily than the sulphates of the other alkalies, and crystallizes in prisms, which resemble the sulphate of soda in appearance, but do not effloresce on exposure to the air. Its taste is saline, without being bitter.

*Sulphate of Ammonia*.—This salt is easily prepared by neutralizing the carbonate of ammonia with dilute sulphuric acid. It crystallizes in long flattened six-sided prisms. It dissolves in two parts of water at 60°, and in an equal weight of boiling water. It is sublimed by heat, but is partially decomposed at the same time. The crystals are composed of 40 parts or one atom of acid, and 17 parts or one atom of ammonia, combined according to Dr Thomson with one atom, and according to Berzelius with two atoms of water.

*Sulphate of Baryta*.—The native sulphate of Baryta, commonly called *heavy spar*, occurs abundantly, chiefly massive, but sometimes in anhydrous crystals, the form of which is variable, being sometimes prismatic and sometimes tabular. Its density is about 4.4. It is easily formed artificially by the way of double decomposition. This salt bears an intense heat without fusing or undergoing any other change, and is one of the most insoluble substances with which chemists are acquainted. It is sparingly dissolved by hot and concentrated sulphuric acid, but is precipitated by the addition of water. According to Dr Thomson it is composed of 78 parts or one atom of baryta, and 40 parts or one atom of sulphuric acid.

*Sulphate of Strontia*.—The sulphate of strontia, the *celestine* of mineralogists, is less abundant than heavy spar. It occurs in prismatic crystals of peculiar beauty in Sicily. Its density is 3.858. As obtained by the way of double decomposition, it is a white heavy powder, very similar to the sulphate of baryta. It requires about 3840 times its weight of boiling water for solution. According to Dr Thomson it consists of 52 parts or one atom of strontia, and one atom of sulphuric acid.

*Sulphate of Lime*.—This salt is easily formed by mixing a solution of the muriate of lime with any soluble sulphate. It occurs abundantly as a natural production. The mineral called *anhydrite* is the anhydrous sulphate of lime ; and all the varieties of *gypsum* are composed of the same salt, united with water. The pure crystallized specimens of gypsum are sometimes called *selenite* ; and the white compact variety is employed in statuary under the name of *alabaster*. The anhydrous compound consists of one atom of acid, and 28 parts or one atom of lime ; and pure gypsum, according to Dr Thomson, is composed of 68 parts or one atom of the sulphate of lime, and 18 parts or two atoms of water. The hydrous salt is deprived of its water by a low red heat, and in this state forms plaster of Paris. Its property of be-

coming hard, when made into a thin paste with water, is owing to the anhydrous sulphate combining chemically with that liquid, and thus depriving it of its fluidity.

The sulphate of lime has hardly any taste. It is considerably more soluble than the sulphates of baryta or strontia, requiring for solution about 500 parts of cold, and 450 of boiling water. Owing to this circumstance, and to its existing so abundantly in the earth, it is frequently contained in spring water, to which it communicates the property called hardness. When freshly precipitated, it may be dissolved completely by dilute nitric acid. It is commonly believed to sustain a white heat without decomposition; but Dr Thomson states, that it parts with some of its acid when heated to redness.

*Sulphate of Magnesia.*—This sulphate, generally known by the name of *Epsom salt*, is frequently contained in mineral springs. It may be made directly by neutralizing dilute sulphuric acid with carbonate of magnesia; but it is procured for the purposes of commerce by the action of dilute sulphuric acid on magnesian limestone, the native carbonate of lime and magnesia.

The sulphate of magnesia has a saline, bitter, and nauseous taste. It crystallizes readily in small quadrangular prisms, which effloresce slightly in a dry air. They are soluble in an equal weight of water at 60°, and in three-fourths of their weight of boiling water. They undergo the watery fusion when heated; and the anhydrous salt is deprived of a portion of its acid at a white heat. The crystals are composed, according to M. Gay-Lussac, of 60 parts or one atom of the dry sulphate, and 63 parts or seven atoms of water.

*Sulphate of Alumina.*—The pure sulphate of alumina is a compound of little interest; but with the sulphate of potassa it forms an interesting double salt, the well-known alum of commerce.

Alum has a sweetish astringent taste. It is soluble in five parts of water at 60° F. and in little more than its own weight of boiling water. The solution reddens litmus paper; but it is doubtful whether this is owing to an excess of acid, or to the weak affinity existing between alumina and sulphuric acid. (Page 314.) It crystallizes readily in octahedrons, or in segments of an octahedron, and the crystals contain almost 50 per cent. of water of crystallization. On being exposed to heat, they froth up remarkably, and part with all the water, forming anhydrous alum, the *alumen ustum* of the pharmacopœia. At a full red heat the alumina is deprived of its acid.

There is some doubt as to the real composition of alum. According to Dr Thomson, it is composed of

Sulphate of alumina,	174	3 atoms
Sulphate of potassa,	88	1 atom
Water,	225	25 atoms

Mr Phillips, on the contrary, regards it as a compound of two atoms of the sulphate of alumina, one atom of the bi-sulphate of potassa, and 22 atoms of water.

The sulphate of alumina forms with the sulphate of ammonia, and with the sulphate of soda, double salts, which are very analogous to common alum.

*Sulphate of Iron.*—The sulphate of the protoxide of iron, commonly called *green vitriol*, is formed by the action of dilute sulphuric acid on metallic iron, (page 118) or by exposing the protosulphuret of iron in fragments to the combined agency of air and moisture. This salt

has a strong, styptic, inky taste. Though neutral in composition, being composed of one atom of each element, it reddens the vegetable blue colours. It is soluble in two parts of cold, and in three-fourths of its weight of boiling water. It occurs in transparent pale green-coloured rhombic crystals, which consist, according to Berzelius, of 76 parts or one atom of the protosulphate, and 63 parts or seven atoms of water. In the anhydrous state it is of a dirty white colour. It is this salt which is employed in the manufacture of the fuming sulphuric acid. (Page 152.)

The protosulphate of iron absorbs oxygen from the air, especially when in solution, by which an insoluble sub-sulphate of the peroxide of iron is generated, consisting, according to Berzelius, of one atom of sulphuric acid, and four atoms of the peroxide.

When a solution of the protosulphate of iron is boiled with a little nitric acid, until the liquid acquires a red colour, and is then evaporated to dryness by a moderate heat, a salt remains, the greater part of which is soluble both in alcohol and water, and which attracts moisture from the atmosphere. The analysis of Berzelius has proved it to be a compound of 40 parts or one atom of the peroxide of iron, and 60 parts or an atom and a half of sulphuric acid. It is, therefore, a sesqui-sulphate of the peroxide of iron.

*Sulphate of Zinc.*—The sulphate of zinc, frequently called *white vitriol*, is the residue of the process for forming hydrogen gas by the action of dilute sulphuric acid on metallic zinc, but is made, for the purposes of commerce, by roasting the native sulphuret of zinc in a reverberatory furnace. It crystallizes by spontaneous evaporation in transparent four-sided prisms, which dissolve in two parts and a half of cold, and are still more soluble in boiling water. It has a strong styptic taste. It reddens vegetable blue colours, though in composition it is a strictly neutral salt, consisting of one atom of each of its elements. The crystals are composed of 82 parts or one atom of the anhydrous sulphate, and 63 parts or seven atoms of water.

*Sulphates of Copper.*—The sulphate of the protoxide of copper has not been obtained in a separate state. The sulphate of the peroxide of copper, the *blue vitriol* employed by surgeons as an escharotic and astringent, may be prepared for chemical purposes by dissolving the peroxide of copper in dilute sulphuric acid; but it is procured for sale by roasting the native sulphuret, so as to bring both its elements to a maximum of oxidation. This salt forms regular crystals of a blue colour, reddens litmus paper, and is soluble in about four of cold, and in two parts of boiling water. According to the researches of Proust, Thomson, and Berzelius, it is composed of 80 parts or one atom of the peroxide of copper, 80 parts or two atoms of acid, and 90 parts or ten atoms of water. It is therefore, strictly, a bisulphate.

When pure potassa is added to a solution of the bisulphate of copper in a quantity which is insufficient for separating the whole of the acid, a pale bluish-green precipitate, the sub-sulphate, is thrown down, which is composed of one atom of acid, and one atom of the peroxide.

The sulphate of copper and ammonia is generated by dropping pure ammonia into a solution of the bisulphate, until the sub-salt at first thrown down is nearly all dissolved. It forms a dark blue solution, from which, when concentrated, crystals are deposited by the addition of alcohol. It may be formed also by rubbing briskly in a mortar two parts of the crystallized bisulphate of copper with three parts of carbonate of ammonia, until the mixture acquires a uniform deep blue



colour. Carbonic acid gas is disengaged with effervescence during the operation, and the mass becomes moist, owing to the water of the blue vitriol being set free.

This compound, which is the *ammoniaret* of copper of the pharmacopœia, contains sulphuric acid, peroxide of copper, and ammonia; but its precise nature has not been determined in a satisfactory manner. It parts gradually with ammonia by exposure to the air.

*Sulphates of Mercury.*—When two parts of mercury are gently heated in three parts of strong sulphuric acid, so as to cause a slow effervescence, a sulphate of the protoxide of mercury is generated. But if a strong heat is employed in such a manner as to excite brisk effervescence, and the mixture is brought to dryness, a pure sulphate of the peroxide results\*. The former is composed of one atom of sulphuric acid and one atom of the protoxide, and the latter of two atoms of acid and one atom of the peroxide. (Thomson.) When this bisulphate, which is the salt employed in making corrosive sublimate, is thrown into hot water, decomposition ensues, and a yellow sub-salt, formerly called *turpeth mineral*, subsides. This salt is composed of one atom of the acid and one atom of the peroxide. The hot water retains some of the sulphate in solution, together with free sulphuric acid.

### Sulphites.

The salts of sulphurous acid have not hitherto been minutely examined. The sulphites of potassa, soda, and ammonia, which are made by neutralizing those alkalies with sulphurous acid, are soluble in water; but most of the other sulphites, so far as is known, are of sparing solubility. The sulphites of baryta, strontia, and lime, are very insoluble, and consequently the soluble salts of these earths decompose the alkaline sulphites.

The stronger acids, such as the sulphuric, muriatic, phosphoric, and arsenic acids, decompose all the sulphites with effervescence, owing to the escape of sulphurous acid, which may easily be recognised by its odour. The nitric acid, by yielding oxygen, converts the sulphites into sulphates.

When the sulphites of the fixed alkalies and alkaline earths are heated strongly in close vessels, a sulphate is generated, and a portion of sulphur sublimes. In open vessels at a high temperature they absorb oxygen, and are converted into sulphates, and a similar change takes place even in the cold, especially when they are in solution. M. Gay-Lussac has remarked, that a neutral sulphite always forms a neutral sulphate when its acid is oxidized; a fact from which it may be inferred, that neutral sulphites consist of one atom of the acid and one atom of the base.

The hyposulphates and hyposulphites are of little importance, and their general character has already been sufficiently described. (Pages 154 and 155.)

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\* Donovan in the *Annals of Philosophy*, vol. xiv.



## SECTION II.

NITRATES. NITRITES. CHLORATES. IODATES.

*Nitrates.*

The nitrates are prepared by the action of nitric acid on metals, on the salifiable bases themselves, or on carbonates. As nitric acid forms soluble salts with all alkaline bases, the acid of the nitrates cannot be precipitated by any reagent. They are readily distinguished from other salts, however, by the three following characters:—1st, by deflagrating with red-hot charcoal; 2d, by their power of dissolving gold leaf on the addition of muriatic acid; 3d, by the evolution of dense, white, acid vapours, which are easily recognised to be nitric acid by their odour, when mixed with strong sulphuric acid.

All the nitrates are decomposed without exception by a high temperature. Some of these salts, of which common nitre is an example, are at first converted with disengagement of oxygen gas into nitrites; and then by continuing the heat, the nitrous acid is resolved almost entirely into oxygen and nitrogen gases, and pure potassa remains. In others, such as the nitrates of baryta and strontia, the acid is apparently changed at once into oxygen and nitrogen, without forming a nitrite. The nitrate of lead, as already mentioned, (p. 136,) yields oxygen and nitrous acid; and the nitrate of palladium, which is decomposed without the application of a strong heat, emits nearly pure nitric acid.

As the nitrates are easily decomposed by heat alone, they must necessarily suffer decomposition by the united agency of heat and combustible matter. The nitrates on this account are much employed as oxidizing agents, and frequently act with greater efficacy even than the nitro-muriatic acid. Thus metallic titanium, which resists the action of these acids, combines with oxygen when heated with nitre. The efficiency of this salt, which is the nitrate usually employed for the purpose, depends not only on the affinity of the combustible for oxygen, but likewise on that of the oxidized body for potassa. The process for oxidizing substances by means of nitre, is called *deflagration*, and is generally performed by mixing the inflammable body with an equal weight of the nitrate, and projecting the mixture in small portions at a time into a red-hot crucible.

All the neutral nitrates of the fixed alkalies and alkaline earths, together with most of the neutral nitrates of the common metals, are composed of one atom of nitric acid, and one atom of a protoxide. Consequently, the oxygen of the oxide and acid in all such salts must be in the ratio of 1 to 5.

The only nitrates found native are those of potassa, soda, lime, and magnesia.

*Nitrate of Potassa.*—This salt is generated spontaneously in the solid, and crystallizes upon its surface, in several parts of the world, and especially in the East Indies, whence the greater part of the nitre used in Britain is derived. In France and Germany, it is prepared artificially from a mixture of common mould or porous calcareous earth with animal and vegetable remains containing nitrogen. When a heap of these materials, preserved moist and in a shaded situation, is moderately exposed to the air, nitric acid is gradually generated, and unites

with the potassa, lime and magnesia, which are commonly present in the mixture. On dissolving these salts in water, and precipitating the two earths by carbonate of potassa, a solution is formed, which yields crystals of nitre by evaporation. The nitric acid is doubtless generated under these circumstances by the nitrogen of the organic matters combining during putrefaction with oxygen of the atmosphere, a change which must be attributed to the affinity of oxygen for nitrogen, aided by that of the nitric acid for alkaline bases.

The nitrate of potassa is a colourless salt, which crystallizes readily in six-sided prisms. Its taste is saline, accompanied with an impression of coolness. It requires for solution seven parts of water at  $60^{\circ}$  F., and its own weight of boiling water. It contains no water of crystallization, but its crystals are never quite free from water lodged mechanically within them. When moderately heated it undergoes the igneous fusion, and like all the nitrates is decomposed by a red heat.

Nitre is chiefly employed in chemistry as an oxidizing agent, and in the formation of nitric acid. Its chief use in the arts is for making gunpowder, which is a mixture of nitre, charcoal, and sulphur. In the East Indies it is employed for the preparation of cooling mixtures;—an ounce of powdered nitre dissolved in five ounces of water reduces its temperature by fifteen degrees. It possesses powerful antiseptic properties, and is therefore much employed in the preservation of meat and animal matters in general.

*Nitrate of Soda.*—This salt is analogous in its chemical properties to the preceding compound.

*Nitrate of Ammonia.*—The nitrate of ammonia may be formed by neutralizing dilute nitric acid by the carbonate of ammonia, and evaporating the solution. This salt may be procured in three different states, which have been described by Sir H. Davy. (Researches concerning the nitrous oxide.) If the evaporation is conducted at a temperature not exceeding  $100^{\circ}$  F., the salt is obtained in prismatic crystals, which are composed, according to the experiments of Davy, Berzelius, and Thomson, of 67 parts or one atom of the neutral nitrate of ammonia, and 9 parts or one atom of water. If the solution is evaporated at  $212^{\circ}$  F., fibrous crystals are procured; and if the heat be gradually increased to  $300^{\circ}$  F., it forms a brittle compact mass on cooling. The fibrous and compact varieties still contain water, the former 8.2 per cent. and the latter 5.7. All these varieties are deliquescent, and very soluble in water.

The change which the nitrate of ammonia undergoes at a temperature varying between 400 and  $500^{\circ}$  of F., has already been explained. When heated to  $600^{\circ}$ , it explodes with violence, being resolved into water, nitrous acid, the deutoxide of nitrogen, and nitrogen. The fibrous variety was found by Sir H. Davy to yield the largest quantity of the protoxide of nitrogen. From one pound of this salt he procured nearly three cubic feet of the gas.

*Nitrate of Baryta.*—This salt is sometimes used as a re-agent, and for preparing pure baryta. It is easily prepared by digesting the native carbonate, reduced to powder, in nitric acid diluted with eight or ten times its weight of water. The salt crystallizes readily by evaporation in transparent octahedrons. Its crystals contain no water of crystallization, and are very apt to decrepitate by heat unless previously reduced to powder. They require twelve parts of water at  $60^{\circ}$  F., and three or four of boiling water for solution. They undergo the igneous fusion in the fire before being decomposed. They are insoluble in alcohol.

*Nitrate of Strontia.*—This salt may be made from strontianite in the same manner as the foregoing compound, to which it is exceedingly analogous. Like all the soluble salts of strontia it gives a blood-red colour to flame. (Page 245.)

*Nitrates of Lime and Magnesia.*—These salts are very deliquescent, and soluble in alcohol. By this character the nitrate of lime is easily distinguished and separated from the nitrates of baryta and strontia. (Page 247.)

*Nitrate of Copper.*—This salt is prepared by the action of nitric acid on copper. (Page 132.) It crystallizes, though with some difficulty, in prisms, which are of a deep blue colour, and deliquesce on exposure to the air. The crystals are composed of 108 parts or two atoms of acid, 80 or one atom of the peroxide, and 126 or 14 atoms of water. (Thomson.) It is therefore strictly a bi-sulphate. The green insoluble sub-salt, procured by exposing the bi-sulphate to heat, contains, exclusive of water, one atom of acid and one atom of the peroxide. When heated to redness it yields pure peroxide of copper.

*Nitrate of Lead.*—This salt is formed by digesting litharge in dilute nitric acid. It crystallizes readily in octahedrons, which are almost always opaque. These crystals are anhydrous. This salt has an acid reaction, but is neutral in composition, consisting of 54 parts or one atom of acid, and 112 or one atom of the protoxide of lead.

A dinitrate of lead, composed of one atom of acid to two atoms of the protoxide, was formed by Berzelius by adding to a solution of the neutral nitrate, a quantity of pure ammonia insufficient for separating the whole of the acid.

*Nitrates of Mercury.*—The protonitrate is conveniently formed by digesting mercury in nitric acid diluted with three or four parts of water, until the acid is saturated, and then allowing the solution to evaporate spontaneously in an open vessel. The solution always contains at first some nitrate of the peroxide, but if metallic mercury is left in the liquid, a pure protonitrate is gradually deposited. The composition of this salt has not been determined in a satisfactory manner; but it probably consists, exclusive of water, of one atom of acid and one atom of the protoxide. This salt dissolves completely in water slightly acidulated with nitric acid, but in pure water a small quantity of a yellow sub-salt is generated.

When mercury is heated in an excess of strong nitric acid, it is dissolved with brisk effervescence owing to the escape of the deutoxide of nitrogen, and transparent prismatic crystals of the pernitrate are deposited as the solution cools. When this salt is put into hot water, a yellow insoluble sub-salt of the peroxide is generated. The former salt is composed, according to Dr Thomson, of one atom of acid to one atom of the peroxide; and M. Grouvelle states the latter to consist of one atom of acid to two atoms of the peroxide. (An. de Ch. et de Ph. vol. xix.)

*Nitrate of Silver.*—Silver is readily oxidized and dissolved by nitric acid diluted with two or three times its weight of water, forming a solution which yields transparent tabular crystals by evaporation. These crystals, which are anhydrous, undergo the igneous fusion when heated, and assume a crystalline texture in cooling. At a red heat it is completely decomposed, and metallic silver remains. When liquefied by heat, and received in small circular moulds, it forms the *lapis infernalis* or *lunar caustic*, employed by surgeons as a cautery. The nitric acid appears to be the agent which destroys the animal texture

and the black stain is owing to the separation of the oxide of silver. It is sometimes employed for giving a black colour to the hair, and is the basis of the indelible ink for marking linens.

The nitrate of silver deliquesces on exposure to the air. It is soluble in its own weight of cold, and in half its weight of hot water. It dissolves also in four times its weight of alcohol. The aqueous solution undergoes little change if preserved in glass vessels; but when paper moistened with it is exposed to light, especially to sun-shine, a black stain is produced, owing to the decomposition of the salt, and reduction of the oxide to the metallic state. This solution is employed by chemists as a test of the presence of chlorine and muriatic acid.

The nitrate of silver, even after fusion, reddens vegetable colouring matters; but it is neutral in composition, consisting of one atom of acid and one atom of the oxide.

### Nitrites.

Little is known with certainty concerning the compounds of nitrous acid with alkaline bases. The nitrite of potassa is probably formed by heating nitre to redness, and removing it from the fire before the decomposition is complete. On adding a strong acid to the product, red fumes of nitrous acid are disengaged, a character which is, of course, common to all the nitrites. Two nitrites of lead have been described in the *Annales de Chimie*, vol. lxxxiii. by M. Chevreul and M. Berzelius. It is possible, however, that these compounds are hyponitrites.

### Chlorates.

The salts of chloric acid are very analogous to the nitrates. As the chlorates of the alkalies, alkaline earths, and most of the common metals, are composed of one atom of chloric acid and one atom of a protoxide, it follows that the oxygen of the latter is to that of the former in the ratio of 1 to 5. The chlorates are decomposed by a red heat, nearly all of them being converted into metallic chlorides, with evolution of pure oxygen gas. (Page 110.) They deflagrate with inflammable substances with greater violence than the nitrates, yielding oxygen with such facility that an explosion is produced by slight causes. Thus a mixture of sulphur with three times its weight of chlorate of potassa explodes when struck between two hard surfaces. With charcoal, and the sulphurets of arsenic and antimony, this salt forms similar explosive mixtures; and with phosphorus it detonates violently by percussion. The mixture employed in the percussion locks for guns consist of sulphur and the chlorate of potassa.

All the chlorates hitherto examined are soluble in water, excepting the proto-chlorate of mercury, which is of sparing solubility. These salts are distinguished by the action of strong muriatic and sulphuric acids, the former of which occasions the disengagement of chlorine and the protoxide of chlorine, and the latter of the peroxide of chlorine.

None of the chlorates are found native. The only ones that require a particular description are the chlorates of potassa and baryta.

*Chlorate of Potassa.* This salt, formerly called *oxymuriate* or

*hyperoxy-muriate of potassa*, is colourless, and crystallizes in four and six-sided scales of a pearly lustre. It is soluble in sixteen times its weight of water at 60° F. and in two and a half of boiling water. It is quite anhydrous, and when exposed to a temperature of 400° or 500° F. undergoes the igneous fusion. On increasing the heat almost to redness, effervescence ensues, and pure oxygen gas is disengaged, phenomena which have been explained in the section on oxygen.

The chlorate of potassa is made by transmitting chlorine gas through a concentrated solution of pure potassa, until the alkali is completely neutralized. The solution which, after being boiled for a few minutes, contains nothing but the muriate and chlorate of potassa, (page 165) is gently evaporated till a pellicle forms upon its surface, and is then allowed to cool. The greater part of the chlorate crystallizes, while the muriate remains in solution. The crystals, after being washed with cold water, may be purified by a second crystallization.

The *chlorate of baryta* is of interest, as being the compound employed in the formation of chloric acid. (Page 171.) The readiest mode of preparing this salt is by the process of Mr Wheeler. On digesting for a few minutes a concentrated solution of the chlorate of potassa with a slight excess of silicated fluoric acid, the alkali is precipitated in the form of an insoluble double fluuate of silica and potassa, while the chloric acid remains in solution. The liquid after filtration is neutralized by carbonate of baryta, which likewise throws down the excess of fluoric acid and silica. The silicated fluoric acid employed in the process is made by conducting fluosilicic acid gas into water.

### Iodates.

From the close analogy in the composition of chloric and iodic acids, it follows that the general character of the iodates must be similar to that of the chlorates. Thus in all neutral proto-iodates the oxygen contained in the oxide and acid is in the ratio of 1 to 5. They form deflagrating mixtures with combustible matters; and on being heated to low redness, oxygen gas is disengaged and a metallic iodide remains. As the affinity of iodine for metals is less energetic than that of chlorine, many of the iodates part with iodine as well as oxygen when heated, especially if a high temperature is employed.

The iodates are easily recognized by the facility with which their acid is decomposed by deoxidizing agents. Thus the sulphurous, phosphorous, muriatic, and hydriodic acids, deprive the iodic acid of its oxygen, and set iodine at liberty. Sulphuretted hydrogen not only decomposes the acid of these salts, but occasions the formation of hydriodic acid by yielding hydrogen to the iodine. Hence an iodate may be converted into a hydriodate by transmitting a current of sulphuretted hydrogen gas through its solution.

None of the iodates have been found native. They are all of very sparing solubility, or actually insoluble in water, excepting the iodates of the alkalies.

*Iodate of potassa*.—This salt is easily procured by adding iodine to a concentrated hot solution of pure potassa, until the alkali is completely neutralized. The liquid which contains the iodate and hydriodate of potassa, (page 180) is evaporated to dryness by a gentle heat, and the residue, when cold, is treated by strong alcohol. The iodate, which is insoluble in that menstruum, is left, while the hydriodate of potassa is dissolved.



All the insoluble iodates may be procured from this salt by double decomposition. Thus the iodate of baryta may be formed by mixing the muriate of baryta with a solution of the iodate of potassa.

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### SECTION III.

*PHOSPHATES. PHOSPHITES. ARSENIATES. ARSENITES.*

#### *Phosphates.*

The neutral salts of phosphoric acid with fixed bases sustain a red heat without decomposition, but they are all fusible at a high temperature. The phosphates of the common metals, at least the greater part of them, are converted into phosphurets by the combined agency of heat and charcoal. The alkaline phosphates are only partially decomposed under these circumstances, and the phosphates of lime, baryta, and strontia, undergo no change. The neutral phosphates, excepting those of potassa, soda, and ammonia, are of sparing solubility in pure water; but they are all dissolved without effervescence in an excess of phosphoric or nitric acid, and are precipitated, for the most part unchanged, from the acid solutions by pure ammonia. Of all the phosphates, those of baryta, lime, and lead, and especially the latter, are the most insoluble.

The presence of a neutral phosphate in solution may be distinguished by the tests already mentioned in the section on phosphorus. (Page 157.) The insoluble phosphates are decomposed when boiled with a strong solution of carbonate of potassa or soda, the acid uniting with the alkali, so as to form a soluble phosphate. The earthy phosphates yield to this treatment with some difficulty, and require continued ebullition.

Several phosphates are met with in the native state, such as those of lime, manganese, iron, uranium, copper, and lead.

*Phosphate of Soda.* Of the alkaline phosphates, that with base of soda is the one generally employed, owing to the facility with which it is obtained in crystals. It is prepared on a large scale in chemical manufactories, by neutralizing the super-phosphate of lime, procured by the action of sulphuric acid on burned bones, (page 156,) with carbonate of soda. The phosphate of lime is separated by filtration, and the clear liquid, after being duly concentrated by evaporation, deposits crystals of the phosphate of soda in cooling. It commonly contains traces of sulphuric acid, from which it may be purified by repeated crystallization. It is customary in this process to employ a slight excess of the alkali, the presence of which facilitates the formation of crystals. On this account the phosphate of soda has commonly an alkaline reaction; but when carefully prepared, Dr Thomson says it is quite neutral.

This salt crystallizes in rhombic prisms, which effloresce on exposure to the air, and require four parts of cold or two of boiling water for solution. According to Dr Thomson, the crystals are composed of 28 parts or one atom of phosphoric acid, 32 or one atom of soda, and 108 or twelve atoms of water.

This salt is employed in medicine as a laxative, and in chemistry as a reagent.

*Phosphate of Soda and Ammonia.* This salt is easily prepared by dissolving one atom of muriate of ammonia and two atoms of phosphate of soda in a small quantity of boiling water. As the liquid cools, prismatic crystals of the double phosphate are deposited, while muriate of soda remains in solution. This salt has been long known by the name of *microcosmic salt*, and is much employed as a flux in experiments with the blow-pipe. When heated it parts with its water and ammonia, and a very fusible biphosphate of soda remains. It is composed of one atom of the phosphate of soda, and one atom of the phosphate of ammonia, united according to Dr Thomson with 16 atoms of water.

*Phosphate of Lime.*—Chemists differ exceedingly as to the number of compounds which phosphoric acid is capable of forming with lime. There seems no doubt, however, from the researches of Berzelius and others, that the phosphate of lime, as it exists in bones, or as obtained by mixing muriate of lime with neutral phosphate of soda in excess, is composed of 28 parts or one atom of phosphoric acid, and 28 or one atom of lime. This is the compound of which many urinary concretions consist.

The biphosphate of lime may be prepared by adding one atom of phosphoric acid to one atom of the phosphate of lime. It is very soluble in water, but does not crystallize. A super-phosphate is also formed by the action of sulphuric acid on phosphate of lime; but whether it is really a biphosphate, or some super-salt with a still larger proportion of acid, is as yet uncertain. The biphosphate exists in the urine.

*Phosphate of Ammonia and Magnesia.*—The simple phosphate of magnesia, which is prepared by mixing a solution of the sulphate of magnesia with phosphate of soda, is of little interest; but the double phosphate is of importance as constituting a distinct species of urinary concretion. It is easily procured by adding carbonate of ammonia and afterwards phosphate of soda to a solution of the sulphate of magnesia, when the double phosphate subsides in the form of minute crystalline grains. This salt is insoluble in pure water; but is dissolved by most acids, even by the acetic, and is precipitated unchanged when the solution is neutralized by ammonia.

The phosphate of magnesia and ammonia, when dried in the air, consists of 48 parts or one atom of the phosphate of magnesia, 45 or one atom of the phosphate of ammonia, and 36 or four atoms of water. On heating this salt, the water and ammonia are dissipated, and a biphosphate of magnesia remains, consisting of 20 parts or one atom of magnesia, and 56 or two atoms of acid. It is insoluble in water, but is dissolved by strong acids. When strongly heated it fuses and forms a white opaque glass.

*Phosphites and Hypophosphites.*—These compounds have hitherto been little examined, and are of no material importance. They do not therefore require a particular description. (Page 159.)

## Arseniates.

All the arseniates are sparingly soluble in water, excepting those of potassa, soda, ammonia, and perhaps of lithia; but they are all dissolved without effervescence by dilute nitric acid as well as most other acids

which do not precipitate the base of the salt, and are thrown down again unchanged by pure ammonia. Most of them bear a red heat without decomposition; but they are all decomposed by being heated to redness along with charcoal, metallic arsenic being set at liberty. The arseniates of the fixed alkalies and alkaline earths require a rather high temperature for reduction; while the arseniates of the common metals, such as those of lead and copper, are easily reduced in a glass tube by means of a spirit-lamp without danger of melting the glass. Of all the arseniates that of lead is the most insoluble.

The soluble arseniates are easily recognised by the tests described in the section on arsenic; (page 271) and the insoluble arseniates, when boiled in a strong solution of the fixed alkaline carbonates, are deprived of their acid, which may then be detected in the usual manner. The free alkali, however, should first be exactly neutralized by pure nitric acid.

The arseniates of lime, nickel, cobalt, iron, copper, and lead, are natural productions.

The arsenic acid unites in two proportions with potassa, soda, and ammonia, forming neutral and bi-salts, all of which, the neutral arseniate of potassa excepted, may be obtained in crystals. They are all formed by adding arsenic acid to the alkaline carbonates. The bin-arseniate of potassa may be formed conveniently by heating to redness equal parts of nitrate of potassa and arsenious acid, and continuing the heat until the effervescence arising from the nitre has ceased.

M. Mitscherlich has ascertained that a close analogy exists between the salts of phosphoric and arsenic acid. So far as his researches have extended, it appears that for every arseniate there is a corresponding phosphate; and that these corresponding salts are analogous in composition, and identical in form. (An. de Ch. et de Ph. vol. xix.)

### *Arsenites.*

The only soluble compounds of arsenious acid and salifiable bases known to chemists, are the arsenites of potassa, soda, and ammonia, which may be prepared by boiling a solution of these alkalies in arsenious acid. The other arsenites are insoluble, or, at most, sparingly soluble in pure water; but they are dissolved by an excess of their own acid, with great facility by nitric acid, and by most other acids with which their bases do not form insoluble compounds. The insoluble arsenites are easily formed by the way of double decomposition.

On exposing the arsenites to heat in close vessels, the arsenious acid is either dissipated in vapour, or converted, with disengagement of some metallic arsenic, into arseniates. Heated with charcoal or black-flux, the acid is reduced with facility. (Page 270.)

The soluble arsenites, if quite neutral, are characterized by forming a yellow arsenite of silver when mixed with the nitrate of that base, and a green arsenite of copper, *Scheele's green*, with the sulphate of copper. When acidulated with acetic or muriatic acid, sulphuretted hydrogen causes the formation of orpiment, an effect which it likewise produces, though slowly, in the arseniates. The insoluble arsenites are all decomposed when boiled in a solution of the carbonate of potassa or soda.

The arsenite of potassa is the active principle of Fowler's arsenical solution.

## SECTION IV.

## CHROMATES. BORATES. FLUATES. FLUOBORATES.

*Chromates.*

The salts of chromic acid are mostly either of a yellow or red colour, the latter tint predominating whenever the acid is in excess. The chromates of the common metals are decomposed by a strong red heat, by which the acid is resolved into the green oxide of chromium and oxygen gas; but the chromates of the fixed alkalies sustain a very high temperature without decomposition. They are all decomposed without exception by the united agency of heat and combustible matter.

The chromates are in general sufficiently distinguished by their colour. They may be known chemically by the following character:—On boiling a chromate in muriatic acid mixed with alcohol, the chromic acid is at first set free, and is then decomposed, a green muriate of the oxide of chromium being generated.

The only native chromate hitherto discovered is the red chromate of lead from Siberia, in the examination of which Vauquelin made the discovery of chromium.

*Chromates of Potassa.*—The chromate of potassa, from which all the compounds of chromium are directly or indirectly prepared, is made by heating to redness the native oxide of chromium and iron, commonly called *chromate of iron*, with an equal weight of the nitrate of potassa, when the chromic acid is generated, and unites with the alkali of the nitre. After digesting the ignited mass in water until the chromate is dissolved, the solution is neutralized by nitric acid, and concentrated by evaporation, in order that the nitrate of potassa should crystallize. The residual liquid is then set aside to evaporate spontaneously, and the chromate is gradually deposited in small prismatic crystals of a lemon-yellow colour.

The chromate of potassa has a cool, bitter, and disagreeable taste. It is soluble to great extent in boiling water, and in twice its weight of that liquid at 60° Fahr. It is insoluble in alcohol. It has an alkaline reaction, and on this account M. Tassaert\*, jun. regards it as a subsalt; but Dr Thomson has proved that it is neutral in composition, consisting of 52 parts or one atom of chromic acid, and 48 parts or one atom of potassa. Its crystals are anhydrous†.

The bichromate of potassa, which is made in large quantity at Glasgow for dyeing, is prepared by acidulating the neutral chromate with sulphuric acid, and allowing the solution to crystallize by spontaneous evaporation. When slowly formed it is deposited in four-sided tabular crystals, which have an exceedingly rich red colour, are anhydrous, and consist of one atom of the alkali, and two atoms of chromic acid. (Thomson.) They are soluble in about ten times their weight of water at 60° F., and the solution reddens litmus paper.

The insoluble salts of chromic acid, such as the chromates of baryta,

\* An. de Ch. et de Ph. vol. xxii.

† Annals of Philosophy, vol. xvi.

lead, protoxide of mercury, and silver, are prepared by mixing the soluble salts of those bases with a solution of the chromate of potassa. The two former are yellow, the third orange-red, and the fourth deep red or purple. The yellow chromate, which consists of one atom of acid, and one atom of oxide, is now extensively used as a pigment.

A dichromate of lead, composed of one atom of chromic acid, and two atoms of the protoxide of lead, may be formed by boiling carbonate of lead with an excess of chromate of potassa. It is of a beautiful red colour, and has been recommended by Mr Badams as a pigment. (*Annals of Philos. N. S.* vol. ix. p. 303.)

### Borates.

As the boracic is a feeble acid, it neutralizes the alkalies in an imperfect manner, and on this account the borates of soda, potassa, and ammonia, have always an alkaline reaction. For the same reason, when the borates are digested in any of the more powerful acids, such as the sulphuric, nitric, or muriatic, the boracic acid is separated from its base. This does not happen, however, at high temperatures; for boracic acid, owing to its fixed nature, decomposes at a red heat all salts, not excepting sulphates, the acid of which is volatile.

The borates of the alkalies are soluble in water, but all the other salts of this acid are of sparing solubility. They are not decomposed by heat, and the alkaline and earthy borates resist the action of heat and combustible matter. They are remarkably fusible in the fire, a property obviously owing to the great fusibility of boracic acid itself.

The borates are distinguished by the following character:—By digesting any borate in a slight excess of strong sulphuric acid, evaporating to dryness, and boiling the residue in strong alcohol, a solution is formed, which has the property of burning with a green flame. (Page 160.)

*Biborate of Soda.*—This salt, the only borate of importance, occurs native in some of the lakes of Thibet and Persia, and is extracted from this source by evaporation. It is imported from India in a crude state, under the name of *Tincal*, which, after being purified, constitutes the *refined borax* of commerce. It is frequently called *sub-borate of soda*, a name suggested by the inconsistent and unphilosophical practice, now quite inadmissible, of regulating the nomenclature of salts merely by their action on vegetable colouring matter. It crystallizes in hexahedral prisms, which effloresce on exposure to the air, and require twenty parts of cold, and six of boiling water, for solution. When exposed to heat, the crystals are first deprived of their water of crystallization, and are then fused, forming a vitreous transparent substance called *glass of borax*. The crystals, according to the analysis of Dr Thomson, are composed of 48 parts or two atoms of boracic acid, 32 or one atom of soda, and 72 or eight atoms of water.

The chief use of borax is as a flux, and for the preparation of boracic acid. The biborate of magnesia is a rare natural production, which is known to mineralogists by the name of *Boracite*.

### Fluates.

The nature of these salts, owing to the uncertainty which exists concerning the constitution of fluoric acid, is as yet involved in ob-



security. I describe them in this place, on the supposition of fluoric acid containing oxygen; but this acid may, with at least equal probability, be regarded as a hydracid. (Page 186.)

The neutral fluates of fixed bases are fusible at a high temperature, and most of those which have been examined may be heated in close vessels to any intensity, if quite dry, without decomposition. The fluates of the alkalies and alkaline earths are not decomposed, so far as is known, by heat and combustible matter; nor does any acid, excepting the boracic, effect their decomposition, provided they are free from moisture. When digested, on the contrary, in concentrated sulphuric, phosphoric, or arsenic acids, the fluoric acid is disengaged, and may be recognised by its property of corroding glass.

Five fluates have hitherto been found native, namely, the fluat of lime, or *fluor spar*, the fluo-silicate of alumina or *topaz*, the fluat of cerium, the double fluat of cerium and yttria, and the double fluat of soda and alumina or *cryolite*. The four latter are very rare minerals, but the former is abundant.

*Fluat of Potassa*.—Potassa unites with fluoric acid in two proportions, forming a fluat and a bifluat, the former of which consists of one atom, and the latter of two atoms of acid, united with one atom of the alkali. The fluat is best formed by heating the bifluat to redness, by which means one atom of fluoric acid is expelled. The fluat is soluble in water, and has an alkaline reaction. It crystallizes with difficulty, and is deliquescent. The bifluat is easily procured by adding to fluoric acid a quantity of potassa insufficient for neutralizing it completely, and concentrating the solution. This salt has an acid reaction, is soluble in water, and is resolved by heat into fluoric acid and fluat of potassa. (Berzelius in the *An. de Ch. et de Ph.* vol. xxvii.)

Fluoric acid forms analogous compounds with soda and ammonia.

*Fluat of Lime*.—This compound, commonly known by the name of *fluor* or *Derbyshire spar*, is frequently found accompanying metallic ores, especially those of tin and lead. It often occurs crystallized either in cubes or some allied forms. The crystals found in the lead mines of Derbyshire are remarkable for the largeness of their size, the regularity of their form, and the variety and beauty of their colours. It may be made artificially by mixing a soluble salt of lime with a solution of the fluat of potassa.

The fluat of lime phosphoresces when heated to redness, and at a very high temperature enters into fusion. According to Dr Thomson, it is composed of 10 parts or one atom of fluoric acid, and 28 parts or one atom of lime.

The native fluor spar is employed in forming vases, as a flux in metallurgic processes, and in the preparation of fluoric acid.

For an account of the other fluates, I may refer to the essay of Berzelius above quoted.

*Fluo-borates*.—The compounds of this acid with salifiable bases are as yet almost entirely unknown. Dr Davy ascertained that it unites with ammoniacal gas in three proportions, forming salts, one of which is solid, and the two others liquid.

## SECTION V.

## CARBONATES.

The carbonates are distinguished from other salts by being decomposed with effervescence, owing to the escape of carbonic acid gas, by nearly all the acids.

All the carbonates, excepting those of potassa, soda, and lithia, may be deprived of their acid by heat. The carbonates of baryta and strontia, and especially the former, require an intense white heat for decomposition; those of lime and magnesia are reduced to the caustic state by a full red heat; and the other carbonates part with their carbonic acid when heated to dull redness.

All the carbonates, excepting those of potassa, soda, and ammonia, are of sparing solubility in pure water; but all of them are more or less soluble in an excess of carbonic acid, owing doubtless to the formation of super-salts.

The former nomenclature of the salts is peculiarly exceptionable as applied to the carbonates. The two well known carbonates of potassa, for example, are distinguished by the prepositions *sub* and *super*, as if the one had an alkaline, and the other an acid re-action; whereas, in fact, according to their action on test paper, they are both sub-salts. I shall adopt the nomenclature which has been employed with other salts, applying the generic name of carbonate to those salts which contain one atom of carbonic acid, and one atom of the base,—compounds which may be regarded as neutral in composition, however they may act on the colouring matter of plants.

Several of the carbonates occur native, among which may be enumerated the carbonates of soda, baryta, strontia, lime, magnesia, manganese, protoxide of iron, copper, lead, and the double carbonate of lime and magnesia.

*Carbonate of Potassa.*—This salt is procured in an impure form by burning land plants, lixiviating their ashes, and evaporating the solution to dryness, a process which is performed on a large scale in Russia and America. The carbonate of potassa, thus obtained, is known in commerce by the names of *potash* and *pearlash*, and is employed in many of the arts, especially in the formation of soap and the manufacture of glass. When derived from this source it always contains other salts, such as the sulphate and muriate of potassa; and therefore, for chemical purposes, should be prepared from cream of tartar, the bitartrate of potassa. On heating this salt to redness, the tartaric acid is decomposed, and a pure carbonate of potassa, mixed with charcoal, remains. The carbonate is then dissolved in water, and, after filtration, is evaporated to dryness in a capsule of platinum or silver.

Pure carbonate of potassa has a taste strongly alkaline, is slightly caustic, and communicates a green to the blue colour of the violet. It dissolves in less than an equal weight of water at 60° F., deliquesces rapidly on exposure to the air, and crystallizes with much difficulty from its solution. In pure alcohol it is insoluble. It fuses at a full red heat, but undergoes no other change. According to the analysis of Dr Wollaston, it is composed of 22 parts or one atom of carbonic acid, and 48 parts or one atom of potassa.

The purity of any given specimen of this salt is conveniently as-

certained by means of sulphuric acid of specific gravity 1.141. Of this acid, 355 grains neutralize 100 grains of pure carbonate of potassa. (Dr Henry.)

The *bicarbonate of potassa* is made by transmitting a current of carbonic acid gas through a solution of the carbonate of potassa. By slow evaporation, the bicarbonate is deposited from the liquid in regular prismatic crystals.

The bicarbonate of potassa, though far milder than the carbonate, is alkaline both to the taste and to test paper. It does not deliquesce on exposure to the air. It requires four times its weight of water at 60° F. for solution, and is much more soluble at 212° F.; but it parts with some of its acid at that temperature. At a low red heat it is converted into the carbonate. From the analysis of Dr Wollaston, the crystals consist of one atom of potassa, two atoms of acid, and one atom of water.

Dr Thomson, in his 'First Principles,' has described a sesqui-carbonate, which\* was discovered by Dr Nimmo of Glasgow. Its crystals are composed of one atom of potassa, an atom and a half of carbonic acid, and six atoms of water.

*Carbonate of Soda.*—The carbonate of soda of commerce is obtained by lixiviating the ashes of sea-weeds. The best variety is known by the name of *barilla*, and is derived chiefly from the *salsola soda* and *salicornia herbacea*. A very inferior kind, known by the name of *kelp*, is prepared from sea-weeds on the northern shores of Scotland. The purest barilla, however, though well fitted for making soap and glass, and for other purposes in the arts, always contains the sulphates and muriates of potassa and soda, and on this account is of little service to the chemist. A purer carbonate is prepared by heating a mixture of sulphate of soda, saw-dust, and lime, in a reverberatory furnace. By the action of the carbonaceous matter, the sulphuric acid is decomposed; its sulphur partly uniting with lime and partly being dissipated in the form of sulphurous acid, while the carbonic acid, which is generated during the process, unites with soda. The carbonate of soda is then obtained by lixiviation and crystallization. It is difficult to obtain this salt quite free from sulphuric acid.

The quantity of real carbonate in the soda of commerce may be conveniently estimated by its neutralizing power. One hundred grains of pure carbonate of soda is neutralized by 460 grains of sulphuric acid of density 1.141.

The carbonate of soda crystallizes in octahedrons with a rhombic base, the acute angles of which are generally truncated. The crystals effloresce on exposure to the air, and, when heated, dissolve in their water of crystallization. By a continued heat they are rendered anhydrous without loss of carbonic acid. They dissolve in about two parts of cold, and in rather less than their weight of boiling water, and the solution has a strong alkaline taste and reaction. According to Dr Thomson the crystals are composed of 22 parts or one atom of carbonic acid, 32 parts or one atom of soda, and 90 parts or ten atoms of water. The water of crystallization is apt to vary according to the temperature at which the crystals are formed.

*Bicarbonate of Soda.*—This salt is made by transmitting a current of carbonic acid gas through a solution of the carbonate, and is deposited in crystalline grains by evaporation. Though still alkaline, it is much milder than the carbonate, and far less soluble, requiring about ten times its weight of water at 60° F. for solution. It is decomposed

partially at 212° F. and is converted into the carbonate by a red heat. It is composed, according to Thomson, of two atoms of acid, one atom of the base, and one atom of water.

*Sesqui-carbonate*.—This compound occurs native on the banks of the lakes of soda in the province of Sukena in Africa, whence it is exported under the name of *Trona*. It was first distinguished from the two other carbonates by Mr Phillips\*, whose analysis corresponds with that of Klaproth. It consists of one atom of soda, an atom and a half of acid, and two atoms of water.

*Carbonate of Ammonia*.—The only method of procuring this salt is by mixing dry carbonic acid over mercury, with twice its volume of ammoniacal gas. It is a dry white volatile powder, of an ammoniacal odour, and alkaline reaction. From the proportion of its constituents by volume, it is easy to infer that it is composed, by weight, of 22 parts or one atom of carbonic acid, and 17 parts or one atom of ammonia.

*Bicarbonate of Ammonia*.—This salt was formed by Berthollet, by transmitting a current of carbonic acid gas through a solution of the common carbonate of ammonia of the shops. On evaporating the liquid by a gentle heat, the bicarbonate is deposited in small six-sided prisms, which have no smell, and very little taste. Berthollet ascertained that it contains twice as much acid as the carbonate.

*Sesqui-carbonate of Ammonia*.—The common carbonate of ammonia of the shops, the *sub-carbonas ammoniæ* of the pharmacopæia, is different from both these compounds. It is prepared by heating a mixture of one part of muriate of ammonia with one part and a half of the carbonate of lime, carefully dried. Double decomposition ensues during the process; muriate of lime remains in the retort, and the sesqui-carbonate of ammonia is sublimed. The carbonic acid and ammonia are, indeed, in proper proportion in the mixture for forming the real carbonate; but from the heat employed in the sublimation, a part of the ammonia is disengaged in a free state.

The salt thus formed, consists, according to the analysis of Mr Phillips, Dr Ure, and Dr Thomson, of 33 parts or an atom and a half of carbonic acid, of 17 parts or one atom of ammonia, and 9 parts or one atom of water. When recently prepared it is hard, compact, semi-transparent, of a crystalline texture, and pungent ammoniacal odour; but if exposed to the air, it loses weight rapidly, and is converted into an opaque brittle mass, which is the bicarbonate.

The *carbonate of Baryta* occurs abundantly in the lead mines of the north of England, where it was discovered by Dr Withering, and has hence received the name of *Witherite*. It may be prepared by way of double decomposition, by mixing a soluble salt of baryta with any of the alkaline carbonates or bicarbonates. It is exceedingly insoluble in distilled water, requiring 4300 times its weight of water at 60° F., and 2300 of boiling water for solution; but when recently precipitated, it is dissolved much more freely by a solution of carbonic acid. It is highly poisonous.

The *carbonate of Strontia*, which occurs native at Strontian in Argyleshire, and is known by the name of *Strontianite*, may be prepared in the same manner as the carbonate of baryta. It is very insoluble in pure water, but is dissolved by an excess of carbonic acid.

*Carbonate of Lime.*—This salt is a very abundant natural production, and occurs under a great variety of forms, such as common limestone, chalk, marble, and Iceland spar, and in regular crystals. It may also be formed by precipitation. Though sparingly soluble in pure water, it is dissolved by carbonic acid in excess. On this account the spring water of limestone districts always contains carbonate of lime, which is deposited when the water is boiled.

*Carbonate of Magnesia.*—This salt is easily prepared by adding carbonate of potassa in slight excess to a hot solution of sulphate of magnesia, and edulcorating the precipitated carbonate with warm water. It requires 2493 parts of cold, and 9000 of hot water for solution. It is so soluble in an excess of carbonic acid that the sulphate of magnesia is not precipitated at all in the cold by the alkaline bicarbonates, or by the sesqui-carbonate of ammonia. On allowing a solution of the carbonate of magnesia in carbonic acid to stand in an open vessel, minute crystals are deposited, which consist of 42 parts or one atom of the carbonate, and 27 parts or three atoms of water. (Dr Henry and Berzelius.)

The native carbonate of magnesia, according to the analysis of Dr Henry and Stromeyer, is similar in composition to the precipitated carbonate.

*Carbonate of Iron.*—Carbonic acid does not form a definite compound with the peroxide of iron, but with the protoxide it constitutes a salt which is an abundant natural production, occurring sometimes massive, and at other times crystallized in rhomboids or hexagonal prisms. This protocarbonate of iron is contained also in most of the chalybeate mineral waters, being held in solution by free carbonic acid; and it may be formed by mixing an alkaline carbonate with the protosulphate of iron. When prepared by precipitation it attracts oxygen rapidly from the atmosphere, and the protoxide of iron, passing into the state of peroxide, parts with carbonic acid. For this reason, the carbonate of iron of the pharmacopœia is of a red colour, and consists chiefly of the peroxide.

*Carbonate of Copper.*—The beautiful green mineral, called *Malachite*, is a carbonate of the peroxide of copper; and a similar compound may be formed from the persulphate by double decomposition, or by exposing metallic copper to air and moisture. According to the analysis of malachite by Mr Phillips, this mineral is composed of 80 parts or one atom of the peroxide of copper, one atom of carbonic acid, and one atom of water. (Journal of Science, vol. iv.)

The blue pigment called *verditer*, said to be prepared by decomposing the nitrate of copper by chalk, is an impure carbonate\*.

*Carbonate of Lead.*—This salt, which is the *white lead* or *ceruse* of painters, occurs native, but may be obtained by double decomposition. It is prepared for the purposes of commerce by exposing coils of thin sheet lead to the vapours of vinegar, when, by the united action of the oxygen of the atmosphere and the acid fumes, the lead is both oxidized and converted into a carbonate.

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\* On the composition and preparation of this pigment the reader may consult the remarks of Mr Phillips in the essay quoted in the text.



## SECTION VI.

## SALTS OF THE HYDRACIDS.

By the expression *salts of the hydracids* is meant those saline compounds, the acid of which contains hydrogen as one of its elements. These salts, owing to the peculiar constitution of their acid, have certain common properties, and may therefore be described advantageously in the same section. Many of the circumstances relative to them have already been mentioned in sufficient detail, partly in the remarks introductory to the study of the metals, (page 230) and partly in the description of the individual metals themselves. I shall, for this reason, treat the salts of the hydracids chiefly in a general manner, giving a particular description of those compounds only, which are possessed of some peculiar interest.

Most of the salts which are composed of a hydracid and a metallic oxide are so constituted, that the oxygen of the oxide contains a quantity of oxygen precisely sufficient for forming water with the hydrogen of the acid. This is true of all the neutral compounds containing a protoxide, without exception, and it likewise holds good in many other cases. Thus, in the soluble muriate of the peroxide of iron, the oxide, which contains an atom and a half of oxygen, is united with an atom and a half of acid; and in the soluble per-muriate of copper, the oxide, which contains two atoms of oxygen, is united with two atoms of acid.

The elements of the salts of the hydracids, as already mentioned, (page 233) are very prone to arrange themselves in a new order. All these salts are exposed to the action of two divellent and three quiescent affinities. In the muriate of soda, for example, the forces which tend to prevent a change, are the attraction of sodium for oxygen; of chlorine for hydrogen, and of muriatic acid for soda; while the opposite affinities are the attraction of chlorine for sodium and of hydrogen for oxygen. The latter always preponderate when heat is employed, because the volatility of water favours the production of that fluid; and in many instances the affinities appear so nicely balanced, that the cohesion of one of the compounds is sufficient to influence the result, as is exemplified by the muriate of soda, which, in the act of crystallizing, is converted into the chloride of sodium.

*Muriates or Hydrochlorates.*

Most of the salts of muriatic acid are soluble in water, and some of them exist only in a state of solution. They are distinguished from other salts by forming the white insoluble chloride of silver when mixed with the nitrate of that base, and by being decomposed with disengagement of muriatic acid fumes by strong sulphuric acid. The decomposition of the muriates, owing to the volatile nature of their acid, is effected by the phosphoric and arsenic acids at the temperature of ebullition.

*Muriate of Potassa and Soda.*—These salts exist only in a state of solution, and are frequently contained in mineral springs. The muriate of soda, as already mentioned in the section on sodium, is the chief constituent of sea-water.

*Muriate of Ammonia.*—This salt, the *sal-ammoniac* of commerce, was formerly imported from Egypt, where it is procured by sublimation from the soot of camel's dung; but it is now manufactured in Europe by several processes. The most usual method is to decompose sulphate of ammonia by the muriate either of soda, or of magnesia. Double decomposition ensues, giving rise in both cases to muriate of ammonia, and to the sulphate of soda, when the muriate of that base is used, or to the sulphate of magnesia when the muriate of magnesia is employed. The *sal-ammoniac* is afterwards obtained in a pure state by sublimation. The sulphate of ammonia may be conveniently procured for this purpose, either by lixiviating the soot of coal, which contains that salt in considerable quantity; or by digesting the impure carbonate of ammonia, procured by exposing bones and other animal matters to a red heat, with gypsum, so as to form an insoluble carbonate of lime, and a soluble sulphate of ammonia.

The muriate of ammonia has a pungent saline taste, and is soluble in three parts of water at 60° F., causing a considerable reduction of temperature during the solution. Boiling water dissolves about an equal weight, and the solution deposits crystals in cooling. At a temperature below redness, it sublimes without fusing or undergoing any change in composition, and condenses on cool surfaces as an anhydrous salt, which attracts humidity in a moist atmosphere, but if pure is not deliquescent.

When muriatic acid gas is mixed with an equal volume of ammonia, both gases disappear entirely, and pure muriate of ammonia results. It hence follows that this salt is composed by weight of 37 parts or one atom of muriatic acid, and 17 parts or one atom of ammonia.

*Muriate of Baryta.*—This compound is best formed by dissolving the carbonate of baryta, either native or artificial, in muriatic acid diluted with three parts of water. It may also be formed by the action of muriatic acid on the hydro-sulphuret of baryta, (page 243) or by heating sulphate of baryta with an equal weight of muriate of lime until fusion takes place, and then dissolving the muriate of baryta, which is generated, and separating it by means of a filter from the sulphate of lime.

The muriate of baryta crystallizes readily in quadrangular tables, when its solution is gently evaporated. The crystals, according to Thomson, consist of 115 parts or one atom of the muriate of baryta, and 9 parts or one atom of water. On heating the crystals to redness two atoms of water are expelled, and 106 parts or one atom of the chloride of barium are left. The crystals, therefore, may be regarded as the chloride of barium with two atoms of water of crystallization, or as the muriate of baryta with one atom of water.

The crystallized muriate of baryta is insoluble in pure alcohol. It requires about two and a half times its weight of water at 60° F. for solution, and is much more soluble in boiling water. The crystals are permanent in the air.

This salt is much employed as a re-agent in chemistry.

The *muriate of strontia* is made in the same manner as the muriate of baryta, from which it is distinguished by forming prismatic crystals, by its solubility in alcohol, and by imparting a red tint to flame. The crystals consist of one atom of the muriate of strontia, and eight atoms of water; and when heated to redness, nine atoms of water are expelled, and one atom of the chloride of strontium remains.

The crystallized muriate attracts humidity from a moist atmosphere,

but, if pure, it is permanent in a dry air. The crystals are exceedingly soluble in boiling water, and require for solution about twice their weight of water at 60° F.

The *muriate of lime* is formed by neutralising muriatic acid with pure marble. This salt is very soluble both in water and alcohol, and deliquesces with rapidity even in a dry atmosphere. It crystallizes, though with considerable difficulty, in prisms, which consist, according to Thomson, of one atom of the muriate of lime, and six atoms of water. When heated, seven atoms of water are expelled and a chloride remains.

The crystallized muriate is the compound which produces such an intense degree of cold when mixed with snow. It is prepared for this purpose by evaporating the solution until a drop of it on falling upon a cold saucer becomes solid.

The *muriate of magnesia* exists in many mineral springs, and is contained abundantly in sea water. When the muriate of soda is separated from sea water by crystallization, an uncrystallizable liquid, called *bittern*, is left, which consists chiefly of the muriate of magnesia, and is much employed in the manufacture of sal-ammoniac for decomposing the sulphate of ammonia.

Muriate of magnesia has a bitter taste, is highly soluble in alcohol and water, and deliquesces with rapidity in the open air. When heated to redness it loses a portion of its acid as well as water.

*Muriate of Iron*.—When iron is dissolved in dilute muriatic acid, a muriate of the protoxide is generated, which yields pale green coloured crystals when the solution is concentrated by evaporation. This salt is much more soluble in hot than in cold water, and is not deliquescent. It absorbs oxygen with rapidity from the air, forming an insoluble muriate of the peroxide. When boiled with a little nitric acid, a soluble muriate of the peroxide is generated, which is of a red colour, crystallizes with difficulty, deliquesces on exposure to the air, and is dissolved by alcohol. It is composed of one atom of the peroxide, and an atom and a half of muriatic acid, being a sesqui muriate.

The black oxide is also dissolved by muriatic acid, forming a dark coloured solution, which may be regarded as a mixture of the muriates of the peroxide and protoxide of iron. (Page 261.)

### *Hydriodates.*

Hydriodic acid unites with the alkalies and alkaline earths, with magnesia, and with the oxides of manganese, zinc, and iron. With several of the metallic oxides, it does not enter into combination. Thus, on mixing the hydriodate of potassa with a salt of mercury or silver, the iodides of those metals are deposited. With the acetate of lead a yellow compound is thrown down, which is an iodide of lead.

The most direct method of forming the hydriodates of the alkalies and alkaline earths, all of which are soluble in water, is by neutralizing those bases with hydriodic acid. The hydriodates of iron and zinc may be made by digesting small fragments of those metals with water in which iodine is suspended.

All the hydriodates are decomposed by sulphuric and nitric acids, or by chlorine, the hydriodic acid being deprived of hydrogen, and the iodine set at liberty, (page 182.) They undergo no change by exposure to the air.

The only hydriodates which have hitherto been found native are those of potassa and soda, the sources of which have already been

mentioned in the section on iodine. Of these salts, the hydriodate of potassa is the most common.

*Hydriodate of Potassa.*—This salt, which is the only hydriodate of importance, exists only in solution; for it is converted in the act of crystallizing into the iodide of potassium. It is exceedingly soluble in boiling water, and requires only two-thirds of its weight of water at 60° F. for solution. It is dissolved freely by alcohol; and when a saturated, hot, alcoholic solution is set aside to cool, the iodide of potassium is deposited in cubic crystals. A solution of the hydriodate of potassa is capable of dissolving a large quantity of iodine, a property which is common to all the hydriodates.

The hydriodate of potassa is easily made by neutralizing hydriodic acid with pure potassa; but in preparing a considerable quantity of the salt, as for medical use, it is desirable to dispense with the preliminary step of making the acid. With this intention the following method, which I have described in the *Edinburgh Medical and Surgical Journal* for July 1825, may be employed with advantage. The process consists in adding to a hot solution of pure potassa as much iodine as it is capable of dissolving, by which means a deep brownish-red coloured fluid is formed, consisting of the iodate and hydriodate of potassa, together with a large excess of free iodine. Through this solution a current of sulphuretted hydrogen gas is transmitted until the free iodine and iodic acid are converted into hydriodic acid, changes which may be known to be accomplished by the liquid becoming quite limpid and colourless. The solution is then gently heated in order to expel any excess of sulphuretted hydrogen, and after being filtered, the pure hydriodic acid is exactly neutralized by pure potassa.

### *Hydrosulphurets or Hydrosulphates.*

Sulphuretted hydrogen forms soluble salts with the alkalies, alkaline earths, and magnesia, most of which are capable of crystallizing. With the alkalies, indeed, if not with other bases, this acid unites in two proportions, forming a hydrosulphate and a bi-hydrosulphate. It may be doubted if sulphuretted hydrogen is capable of uniting with any of the oxides of the common metals; for when their salts are mixed with the hydrosulphate of potassa, a precipitate takes place, which in most, if not in all cases, is the sulphuret of a metal, and not the hydrosulphate of its oxide. Thus, by the action of the hydrosulphate of potassa on the nitrate of lead, copper, bismuth, silver, or mercury, a nitrate of potassa is formed, water is generated, and a metallic sulphuret subsides. The precipitates occasioned by hydrosulphate of potassa in a salt of iron, zinc, and manganese, may also be regarded as sulphurets; for though sulphuric acid decomposes these compounds with evolution of sulphuretted hydrogen, it does not follow that the acid had previously existed in them.

As sulphuretted hydrogen is a weak acid, and is naturally gaseous, its salts are decomposed by most other acids, such as the sulphuric, muriatic, and acetic acids, with disengagement of sulphuretted hydrogen gas, a character by which all the hydrosulphates are easily recognised. They are decomposed, likewise, by chlorine and iodine, with separation of sulphur, and formation of a muriate or hydriodate. When recently prepared, they form solutions which are colourless, or nearly so; but on exposure to the air, oxygen gas is absorbed, a portion of its acid is deprived of its hydrogen, and a sulphuretted hydrosulphate

of a yellow colour is generated. By continued exposure, the whole of the sulphuretted hydrogen is decomposed, water and hypo-sulphurous acid being produced.

The hydrosulphates of baryta and strontia, prepared by dissolving the sulphurets of barium and strontium in water, are sometimes used in preparing the salts of those bases. The hydrosulphates of potassa and ammonia are employed as re-agents.

*Hydrosulphate of Potassa.*—This salt is made by transmitting a current of sulphuretted hydrogen gas into a solution of pure potassa, contained in a Woulfe's apparatus, and continuing the operation as long as the gas is absorbed. When all the alkali is combined with sulphuretted hydrogen, it is no longer able to precipitate a salt of magnesia. If the alkali is completely saturated with the gas, the resulting compound, though it has still an alkaline reaction, is a bi-hydrosulphate. This salt has an alkaline bitter taste, and crystallizes in six-sided prisms, which are deliquescent and soluble in alcohol as well as water.

*Hydrosulphate of Ammonia.*—This salt is made in the same manner as the preceding compound. It may be procured in white acicular crystals by mixing together sulphuretted hydrogen and ammoniacal gases in a dry vessel. As the crystals are very volatile, the vessel in which the combination is effected should be kept cool by ice.

*Hydroseleniates.*—These salts have been little examined, owing to the scarcity of selenium. The researches of Berzelius have demonstrated, however, that hydroselenic acid forms with the alkalies soluble compounds, which are very analogous in their chemical relations to the hydrosulphates, and which precipitate the salts of the common metals, giving rise in most, if not in all cases, to the formation of a metallic seleniuret.

## Hydrocyanates.

The hydrocyanic acid unites with alkalies and alkaline earths, and probably with several other bases; but these compounds have as yet been studied in a very imperfect manner. The hydrocyanate of potassa is the best known. It is generated by the decomposition of water when the cyanuret of potassium is put into that fluid, and may be made directly by mixing hydrocyanic acid with a solution of potassa. M. Robiquet recommends that it should be prepared by exposing the ferrocyanate of potassa to a long-continued red heat, by which means the ferrocyanic acid is decomposed, and a dark mass, consisting of the cyanuret of potassium, mixed with charcoal and iron, remains in the crucible. This process succeeds well if carefully performed; but it is difficult to destroy the whole of the ferrocyanic acid, without decomposing at the same time the cyanuret of potassium. If the decomposition of the ferrocyanate is complete, the residue should form a colourless solution, which does not produce Prussian blue with a salt of the peroxide of iron.

The hydrocyanate of potassa appears to exist only in solution; for when evaporated to dryness, it is converted into the cyanuret of potassium, a compound which is far less liable to spontaneous decomposition than hydrocyanic acid, and is capable of supporting a very high temperature in close vessels without change. It is deliquescent, and highly soluble in water. The solution gives a green colour to violets, and has an alkaline taste, accompanied with the flavour and a faint odour of hydrocyanic acid. It is decomposed by nearly all the acids,



even by the carbonic, and on this account should be preserved in well-closed vessels. It acts upon the animal system in the same manner as hydrocyanic acid, and MM. Robiquet and Villermé have proposed its employment in medical practice, as being more uniform in strength, and less prone to decomposition than hydrocyanic acid. (Jour. de Physiologie, vol. iii.)

### *Ferrocyanates.*

The neutral ferrocyanates, so far as is known, appear to be formed in the same manner as the salts of the hydracids in general; namely, the hydrogen of the acid is in exact proportion for forming water with the oxygen of the salifiable base with which it is united. Thus, the ferrocyanate of potassa is composed of one atom of ferrocyanic acid, which contains two atoms of hydrogen, (page 215,) and two atoms of potassa. With the alkalies and alkaline earths this acid forms soluble compounds; but it precipitates nearly all the salts of the common metals, giving rise either to the ferrocyanate of an oxide or the ferrocyanuret of a metal.

*Ferrocyanate of Potassa.*—This salt, sometimes called *triple prussiate of potash*, is prepared by digesting pure ferrocyanate of the peroxide of iron in potassa until the alkali is neutralized, by which means the peroxide of iron is set free, and a yellow liquid is formed, which yields crystals of the ferrocyanate of potassa by evaporation. This salt is made on a large scale in the arts by igniting dried blood or other animal matters, such as hoofs and horns, with potash and iron. By the mutual reaction of these substances at a high temperature, the ferrocyanuret of potassium, consisting of one atom of the radical of ferrocyanic acid, (page 215,) and two atoms of potassium, is generated. Such at least is inferred to be the product; for on digesting the residue in water, a solution of the ferrocyanate of potassa is obtained.

The ferrocyanate of potassa is a perfectly neutral salt, which is soluble in less than its own weight of water, and forms large transparent, lamellated, crystals of a lemon-yellow colour. It is inodorous, has a slightly bitter taste, but quite different from that of hydrocyanic acid, and is permanent in the air. When heated to 212° F. or even below that temperature, each atom of the salt parts with two atoms of water, leaving one atom of the ferrocyanuret of potassium. The water, indeed, is disengaged with such facility, that Berzelius regards the crystals as consisting of the ferrocyanuret of potassium combined with two atoms of water of crystallization. (An. de Ch. et de Ph. vol. xv.) On heating the dry compound to full redness in close vessels, decomposition takes place, nitrogen gas is disengaged, and cyanuret of potassium mixed with carburet of iron remains in the retort.

The ferrocyanate of potassa is employed in the preparation of several compounds of cyanogen, and as a re-agent for detecting the presence of iron and other substances.

The *ferrocyanate of baryta* is prepared by digesting purified Prussian blue with a solution of pure baryta. It is soluble in water, and forms yellow crystals by evaporation. It is used in the formation of ferrocyanic acid.

When the ferrocyanate of potassa is mixed in solution with a salt of lead, a white precipitate subsides, which Berzelius has proved to be similar in composition to the ferrocyanuret of potassium, consisting of one atom of the radical of ferrocyanic acid, and two atoms of lead.

With salts of mercury and silver, analogous compounds, likewise of a white colour, are generated. With a per-salt of copper, the ferrocyanate of potassa causes a brownish-red precipitate, which appears to be the ferrocyanate of the peroxide of copper.

The *ferrocyanate of the peroxide of iron*, which is formed by mixing the ferrocyanate of potassa with a per-salt of iron in slight excess, and washing the precipitate with water, is characterized by an intensely deep blue colour, and is the basis of the beautiful pigment called *Prussian blue*. It is insipid and inodorous, insoluble in water, and is not decomposed by dilute muriatic or sulphuric acids. Concentrated muriatic acid, by the aid of heat, separates the acid, and strong sulphuric acid renders it white—a change, the nature of which has not been explained. The alkalies and alkaline earths decompose it readily, uniting with the ferrocyanic acid and separating the peroxide of iron. The peroxide of mercury, as already mentioned, (page 297) effects the complete decomposition of the salt, forming the cyanuret of mercury. Very complicated changes are produced by an elevated temperature. On heating the ferrocyanate to redness in a close vessel, a considerable quantity of water and carbonate of ammonia, together with a small portion of hydrocyanate of ammonia are generated; while a carburet of iron remains in the retort—phenomena which, in conjunction with the facts above stated, leave no doubt of this compound containing ferrocyanic acid and the peroxide of iron. The precise proportion of its constituents has not been satisfactorily determined; but it most probably consists of one atom of the peroxide, and an atom and a half of the acid.

Prussian blue, the discovery of which was made in 1710, has been studied by several chemists, especially by Proust, (An. de Ch. tome LX.) and by Berzelius, Porrett, and Robiquet, to whose essays I referred while describing the ferrocyanic acid. The colouring matter of this pigment is ferrocyanate of the peroxide of iron, which is mixed with alumina and peroxide of iron, together with the sub-sulphates of one or both of those bases. It is prepared by heating to redness dried blood, or other animal matters, with an equal weight of pearlash, until the mixture has acquired a pasty consistence. The residue, which consists chiefly of cyanuret of potassium and carbonate of potassa, is dissolved in water, and after being filtered, is mixed with a solution of two parts of alum and one part of the protosulphate of iron. A dirty greenish precipitate ensues, which absorbs oxygen from the atmosphere, and passes through different shades of green and blue, until at length it acquires the proper colour of the pigment.

The chemical changes which take place in this process are of a complicated nature. The precipitate, which is at first thrown down, is occasioned by the potash, and consists chiefly of alumina and the protoxide of iron. The ferrocyanic acid is generated by the protoxide reacting upon some of the hydrocyanic acid, so as to form water and cyanuret of iron, which then unites with undecomposed hydrocyanic acid. The ferrocyanic acid, thus produced, combines with oxide of iron; and when the latter has attained its maximum of oxidation, the compound acquires its characteristic blue tint. Dr Thomson, knowing the protoxide to be necessary to the success of the operation, concludes that this oxide enters into the composition of the Prussian blue; but here this acute chemist is certainly in error. The only use of the protoxide of iron is to convert the hydrocyanic into ferrocyanic acid; a purpose for which its presence is essential, because the per-

oxide of iron does not produce this effect, or at least in a very slow and imperfect manner. In every good specimen of Prussian blue which I have examined, the ferrocyanic acid was in combination with the peroxide of iron only.

*Sulphocyanates.*—The salts of sulphocyanic acid have been chiefly studied by Mr Porrett and Berzelius. The sulpho-cyanate of potassa, which is the most interesting and the best known of these compounds, is prepared by heating the ferrocyanate of potassa with sulphur, a process first proposed by Grotthus, and since modified by M. Vogel and myself. The most convenient method of performing it, is to mix the ferrocyanate, in fine powder, with an equal weight of sulphur, and to place the mixture, contained in a porcelain capsule, just above a pan of burning charcoal, so that it may be exposed to a very strong heat, but short of redness. The mixture is speedily fused, takes fire, and burns briskly for one or two minutes, during which it should be well stirred. The combustion then ceases spontaneously, and the dark-coloured residue, consisting of unburned sulphur, sulphocyanuret of potassium, and sulphuret of iron, on being dissolved in water and filtered, yields a very pure and neutral sulphocyanate of potassa. To insure the decomposition of all the ferrocyanate of potassa, the mass may be allowed to remain in a fused condition for a few minutes after the combustion has ceased, previously to withdrawing it from the fire.

In this process the iron and cyanogen of the ferrocyanate combine with separate portions of sulphur, forming a sulphuret of iron and a sulphuret of cyanogen, the latter of which unites with potassium. On the addition of water, a portion of that liquid is decomposed, and the sulphocyanate of potassa is generated.

The sulphocyanate of potassa, (and most of the salts of this group have probably a similar constitution,) contains one atom of the acid, and one atom of the oxide; so that the oxygen and hydrogen are in due proportion for combining. This salt, indeed, exists only in a liquid state; for the crystals which are deposited from a concentrated solution, when separated from the adhering moisture by bibulous paper, do not contain either water or its elements, but are a pure sulphocyanuret of potassium. The crystals are very deliquescent on exposure to the air, and dissolve freely in water, yielding a solution which is quite neutral. In form, taste, and fusibility, they are very analogous to nitre.

The sulphocyanate of potassa is employed in preparing the sulphocyanic acid, and as a test for detecting the presence of the peroxide of iron.

## PART III.

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### ON ORGANIC CHEMISTRY.

**T**HE department of organic chemistry comprehends the history of those compounds which are solely of animal or vegetable origin, and which are hence called organic substances. These bodies, viewed collectively, form a remarkable contrast with those of the mineral kingdom. Such substances in general are characterized by containing some principle peculiar to each. Thus the presence of nitrogen in the nitric, and of sulphur in the sulphuric acid, establishes a wide distinction between these substances; and although in many instances two or more inorganic bodies consist of the same elements, as is exemplified by the compounds of sulphur and oxygen, or of nitrogen and oxygen, they are always few in number, and are distinguished by a well-marked difference in the proportion in which they are united. The products of animal and vegetable life, on the contrary, consist essentially of the same elementary principles, the number of which is very limited. They are nearly all composed of carbon, hydrogen, and oxygen, in addition to which some of them contain nitrogen. Besides these, portions of phosphorus, sulphur, iron, silica, potassa, lime, and other substances of a like nature may sometimes be detected; but their quantity is exceedingly minute when compared with the principles above mentioned. In point of composition, therefore, most organic substances differ only in the proportion of their constituents, and on this account may not unfrequently be converted into one another.

The constitution of organic bodies is subject to the general laws of chemical union; but chemists are not agreed as to the mode in which they conceive the elements to be combined. Berzelius, for instance, is of opinion that the elements of organic substances do not form binary compounds in the same manner as the constituents of inorganic bodies, (page 313) but are united indiscriminately with one another. Thus alcohol, which consists of three atoms of hydrogen, one atom of oxygen, and two atoms of carbon, is supposed by that chemist to consist of all these six atoms, combined directly with each other, the oxygen belonging as much to the carbon as to the hydrogen. (*Annals of Philosophy*, vol. iv.) This opinion, however, is not universally adopted. Gay-Lussac, for instance, regards alcohol as a compound of olefiant gas and water, a view which is not only justified by the number of atoms contained in that compound, but which, as I conceive, harmonizes with the constitution of other bodies better than that of Berzelius. It may therefore be admitted as probable, that the elements of organic substances are arranged in a similar manner.

Organic substances, owing to the energetic affinities with which

their elements are endowed, are very prone to spontaneous decomposition. The prevailing tendency of carbon and hydrogen is to appropriate to themselves so much oxygen as shall convert them into carbonic acid and water; and hence, in whatever manner these three elements may be mutually combined in a vegetable substance, they are always disposed to resolve themselves into the compounds just mentioned. If at the time this change occurs there is an insufficient supply of oxygen to oxidize the hydrogen and carbon completely, then, in addition to carbonic acid and water, carbonic oxide and carburetted hydrogen gases will probably be generated. One or both of these combustible products must in every case be formed, except when oxygen is freely supplied from extraneous sources; because organic bodies are so constituted that their oxygen is never in sufficient quantity for converting the carbon into carbonic acid, and the hydrogen into water.

If substances composed of oxygen, hydrogen, and carbon, are liable to spontaneous decomposition, that tendency becomes much stronger when, in addition to these elements, nitrogen is annexed. Other and powerful affinities are then superadded to those above enumerated, and especially that of hydrogen for nitrogen. A body which contains these principles is peculiarly liable to change, and the usual products are water, carbonic acid, and ammonia, the two latter having a strong attraction for each other, being always in combination.

Another circumstance which is characteristic of organic products is the impracticability of forming them artificially by direct union of their elements. Thus no chemist has hitherto succeeded in causing oxygen, hydrogen, and carbon to unite so as to form gum or sugar. When these principles are made to combine by chemical means, they always give rise to the production of water and carbonic acid.

Animal and vegetable substances are all decomposed by a red heat, and nearly all are partially affected by a temperature far below ignition. When heated in the open air, or with substances which yield oxygen freely, they burn, and are converted into water and carbonic acid; but if exposed to heat in vessels from which the atmospheric air is excluded, very complicated products ensue. A compound, consisting of carbon, hydrogen, and oxygen, yields water, carbonic acid, carbonic oxide, carburetted hydrogen of various kinds, and probably pure hydrogen. Besides these products, some acetic acid is commonly generated, together with a volatile oil which has a dark colour and burnt odour, and is hence called empyreumatic oil. An azotized substance, in addition to these, yields ammonia, cyanogen, and perhaps free nitrogen.

From the foregoing remarks, it appears that organic products are characterized by the following circumstances:—1st, by being composed of the same elements; 2d, by the facility with which they undergo spontaneous decomposition; 3d, by the impracticability of forming them by direct union of their principles; 4th, by being decomposed at a red heat.

### *Vegetable Chemistry.*

All bodies which are of vegetable origin are termed vegetable substances. They are nearly all composed of oxygen, hydrogen, and carbon, and in a few of them nitrogen is likewise present. Every distinct compound which exists ready formed in plants, is called a



*proximate* or *immediate principle* of vegetables. Thus sugar, starch, and gum, are proximate principles. Opium, though obtained from a plant, is not a proximate principle; but it consists of several proximate principles mixed more or less intimately with one another.

The proximate principles of vegetables are sometimes distributed over the whole plant, while at others they are confined to a particular part of it. The methods by which they are procured are very variable. Thus, gum exudes spontaneously, and the saccharine juice of the maple tree is obtained by incisions made in the bark. In some cases a particular principle is mixed with such a variety of others, that a distinct process is required for its separation. Of such processes consists the *proximate analysis* of vegetables. Sometimes a substance is separated by mechanical means, as in the preparation of starch. On other occasions, advantage is taken of the volatility of a compound, or of its solubility in some particular menstruum. Whatever method is employed, it should be of such a nature as to occasion no change in the composition of the body to be prepared.

The reduction of the proximate principles into their simplest parts, constitutes their *ultimate analysis*. By this means chemists ascertain the quantity of oxygen, carbon, and hydrogen, present in any compound. The former method of performing this operation was by what is termed *destructive distillation*; that is, by exposing the compounds to a red heat in close vessels, and collecting all the products. So many different substances, however, are procured in this way, such as water, carbonic acid, carbonic oxide, carburetted hydrogen, and the like, that it is almost impossible to arrive at a satisfactory conclusion. A more simple and effectual method was proposed by Gay-Lussac and Thénard in the second volume of their celebrated *Recherches Physico-Chimiques*. The object of their process, which is applicable to the ultimate analysis of animal, as well as of vegetable substances, is to convert the whole of the carbon into carbonic acid, and the hydrogen into water, by means of some compound which contains oxygen in so loose a state of combination, as to give it up to those elements at a red heat.

The agent first employed by these chemists was the chlorate of potassa. This substance, however, is liable to the objection that it not only gives oxygen to the substance to be analyzed, but is itself decomposed by heat. On this account it is now very rarely employed in ultimate analysis, the peroxide of copper, likewise proposed by Gay-Lussac and Thénard, having been substituted for it. This oxide, if alone, may be heated to whiteness without parting with oxygen; whereas it yields oxygen readily to any combustible substance with which it is ignited. It is easy, therefore, by weighing it before and after the analysis, to discover the precise quantity of oxygen which has entered into union with the carbon and hydrogen contained in the substance submitted to examination.

The ultimate analysis of organic bodies is one of the most delicate operations with which the analytical chemist can be engaged. The chief cause of uncertainty in the process arises from the presence of moisture, which is retained by some animal and vegetable substances with such force that it can be expelled only by a temperature which endangers the decomposition of the compound itself. The best mode of drying organic matters for the purpose, is by confining them with sulphuric acid under the exhausted receiver of an air-pump, and exposing them at the same time to a temperature of  $212^{\circ}$  F.—a method adopted by Berzelius, and for which a neat apparatus has been de-

scribed by Dr Prout. (*Annals of Philosophy*, vol. vi. p. 272.) Another source of difficulty is occasioned by atmospheric air within the apparatus, owing to the presence of which nitrogen may be detected in the products, without having been contained in the substance analyzed.

But though the ultimate analysis of organic substances is difficult in practice, in theory it is exceedingly simple. It consists in mixing three or four grains of the body to be analyzed with about 200 grains of the peroxide of copper, heating the mixture to redness in a glass tube, and collecting the gaseous products in a graduated glass jar over mercury. From the quantity of carbonic acid procured by measure, its weight may readily be inferred; (page 144) and from this, the quantity of carbonaceous matter is calculated, by recollecting that every 22 grains of the acid contain 16 of oxygen and 6 of carbon.

In order to ascertain the quantity of hydrogen, the gaseous products are transmitted through a tube filled with fragments of the fused chloride of calcium, which absorbs all the watery vapour, and by its increase in weight indicates the precise quantity of that fluid generated. Every nine grains of water thus collected correspond to one grain of hydrogen and eight of oxygen.

If the quantity of oxygen contained in the carbonic acid and water corresponds precisely to that lost by the oxide of copper, it follows that the organic substance itself was free from oxygen. But if, on the other hand, more oxygen exists in the products than was lost by the copper, it is obvious that the difference indicates the amount of oxygen contained in the subject of analysis.

If nitrogen enters into the constitution of the organic substance, it will pass over in the gaseous state, mixed with carbonic acid. Its quantity may be ascertained by removing the carbonic acid by means of a solution of pure potassa.

It need scarcely be observed, that if the analysis has been successfully performed, the weight of the different products, added together, should make up the exact weight of the organic substance employed.

In analyzing an animal or vegetable fluid, the foregoing process will require a slight modification. If the fluid is of a fixed nature, it may be made into a paste with the oxide of copper, and heated in the usual manner. But if it is volatile, a given weight of its vapour is conducted over the peroxide of copper heated to redness in a glass tube.

The constitution of vegetable substances is not yet sufficiently known to admit of their being classified in a purely scientific order. The chief data hitherto furnished towards forming a systematic arrangement, are derived from a remarkable agreement between the composition and general properties of several vegetable compounds, first noticed by Gay-Lussac and Thénard. (*Recherches*, vol. ii.) From the ultimate analysis of a considerable variety of proximate principles, these chemists draw the three following conclusions:—1st, A vegetable substance is always acid, when it contains more than a sufficient quantity of oxygen for converting all its hydrogen into water; 2dly, It is always resinous, oily, or alcoholic, &c. when it contains less than a sufficient quantity of oxygen for combining with the hydrogen; and, 3dly, It is neither acid nor resinous, but in a state analogous to sugar, gum, starch, or the woody fibre, when the oxygen and hydrogen, which it contains, are in the exact proportion for forming water.

These laws, indeed, can hardly be regarded as rigidly exact, nor do they include the vegetable products containing nitrogen; but as chemists are possessed of no better principle of classification, I shall follow M. Thénard in making them, to a certain extent, the basis of my arrangement. I shall accordingly arrange the proximate principles of plants in five divisions. The first includes the vegetable acids; the second the vegetable alkalies; the third comprises those substances which contain an excess of hydrogen; the fourth includes those, the oxygen and hydrogen of which are in proportion for forming water; and the fifth comprehends those bodies which, so far as is known, do not belong to either of the other divisions.

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## SECTION I.

### VEGETABLE ACIDS.

Those compounds are regarded as vegetable acids which possess the properties of an acid, and are derived from the vegetable kingdom. These acids, like all organic principles, are decomposed by a red heat. They are in general less liable to spontaneous decomposition than other vegetable substances; a circumstance which probably arises from the large proportion of oxygen which they contain. They are nearly all decomposed by concentrated hot nitric acid, by which they are converted into carbonic acid and water.

#### *Acetic Acid.*

The acetic acid exists ready formed in the sap of many plants, either free or combined with lime or potassa; it is generated during the destructive distillation of vegetable matter, and is an abundant product of the acetous fermentation.

Common vinegar, the acidifying principle of which is the acetic acid, is commonly prepared in this country by fermentation from an infusion of malt, and in France from the same process taking place in weak wine. Vinegar, thus obtained, is a very impure acetic acid, containing the saccharine, mucilaginous, and other matters existing in the fluid from which it is prepared. It is separated from these impurities by distillation. Distilled vinegar was formerly called *acetous acid*, on the supposition of its differing chemically from the strong acetic acid; but it is now admitted that distilled vinegar is real acetic acid merely diluted with water, and commonly containing a small portion of empyreumatic oil, formed during the distillation, from which it receives a peculiar flavour. It may be rendered stronger by exposure to cold, when a considerable part of the water is frozen, while the acid remains liquid.

The distilled vinegar, which is now generally employed for chemical purposes, is prepared by the distillation of wood, and is sold under the name of *pyroligneous acid*. When first made it is very impure, and of a dark colour, holding in solution tar and volatile oil; but it may be purified by filtration through animal charcoal. The method employed for purifying it at Glasgow, where it is made in large quantity, has not to my knowledge been made public.

Concentrated acetic acid is best obtained by decomposing the acetates either by sulphuric acid, or in some instances by heat. A convenient process is to distil acetate of potassa with half its weight of concentrated sulphuric acid, the recipient being kept cool by the application of ice. The acid is at first contaminated with sulphurous acid, but by mixing it with a little peroxide of manganese, and re-distilling, it is rendered quite pure. A strong acid may likewise be procured from the bin-acetate of copper by the sole action of heat. The acid when first collected has a greenish tint, owing to the presence of copper, from which it is freed by a second distillation. The density of the product varies from 1.056 to 1.08, the lightest acid being procured towards the end of the process. MM. Derosnes, indeed, have remarked that the liquid which passes over towards the end of the process is lighter than water, and contains very little acetic acid. On neutralizing the latter with pure solid potassa, and distilling by a gentle heat, they procured an ethereal fluid, to which they applied the term of *pyro-acetic ether*.

Strong acetic acid is exceedingly pungent, and even raises a blister when kept for some time in contact with the skin. It has a very sour taste and an agreeable refreshing odour. Its acidity is well marked, as it reddens litmus paper powerfully, and forms neutral salts with the alkalis. It is exceedingly volatile, rising rapidly in vapour at a moderate temperature, without undergoing any change. Its vapour is inflammable, and burns with a white light. In its most concentrated form it is an atomic compound of one atom of water, and one atom of acid, and in this state it crystallizes when exposed to a low temperature, retaining its solidity until the thermometer rises to 50° F. It is decomposed by being passed through red-hot tubes; but owing to its volatility, a large quantity of it escapes decomposition.

The atomic weight of acetic acid, as deduced by Dr Thomson from his analysis of the acetates of soda and lead, is 50; and by comparing this number with the analysis of Berzelius, the acid itself is inferred to consist of

Carbon,	. . . .	24 or 4 atoms
Oxygen,	. . . .	24 3 atoms
Hydrogen,	. . . .	2 2 atoms.

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50

The only correct mode of estimating the strength of acetic acid is by its neutralizing power. Its specific gravity is no criterion, as will appear from the following table. (Thomson's First Principles, vol. ii. p. 135.)

Table exhibiting the density of acetic acid of different strengths.

<i>Acid.</i>		<i>Water.</i>			<i>sp. gr. at 60° F.</i>
1 atom	+	1 atom	.	.	1.06296
1	+	2	.	.	1.07060
1	+	3	.	.	1.07080
1	+	4	.	.	1.07132
1	+	5	.	.	1.06820
1	+	6	.	.	1.06708
1	+	7	.	.	1.06349
1	+	8	.	.	1.05974
1	+	9	.	.	1.05794
1	+	10	.	.	1.05439

The acetic is distinguished from all other acids by its flavour, odour, and volatility. Its salts, which are called *acetates*, are all soluble in hot and most of them in cold water, and destroyed by a high temperature, and are decomposed by sulphuric acid.

*Acetate of potassa*.—This salt is made by neutralizing carbonate of potassa with acetic acid, or by decomposing acetate of lime with sulphate of potassa. When cautiously evaporated it forms irregular crystals, which are obtained with difficulty, owing to the deliquescent property of the salt. According to Dr Thomson, the crystals are composed of one atom of the neutral acetate of potassa, and two atoms of water. It is commonly prepared for pharmaceutic purposes by evaporating the solution to dryness, and heating the residue so as to cause the igneous fusion. On cooling it becomes a white crystalline foliated mass, which is generally alkaline.

This salt is highly soluble in water, and requires twice its weight of boiling alcohol for solution.

Dr Thomson procured a bin-acetate by mixing acetic acid and carbonate of potassa in the proportion of two atoms of the former to one atom of the latter. On confining the solution along with sulphuric acid under the exhausted receiver of an air-pump, the bin-acetate was deposited in large transparent flat plates. The crystals contain six atoms of water, and deliquesce rapidly on exposure to the air.

The *acetate of soda* is prepared in large quantity by manufacturers of the pyroligneous acid by neutralizing the impure acid with chalk, and then decomposing the acetate of lime by sulphate of soda. It crystallizes readily by gentle evaporation, and its crystals, which are not deliquescent, are composed of 50 parts or one atom of acetic acid, 32 parts or one atom of soda, and 54 parts or six atoms of water. (Berzelius and Thomson.) When heated to 550° F., it is deprived of its water, and undergoes the igneous fusion without parting with any of its acid. At 600° F. decomposition takes place.

The acetate of soda is much employed for the preparation of concentrated acetic acid.

The *acetate of ammonia* is made by neutralizing the common carbonate of ammonia with acetic acid. It crystallizes with difficulty in consequence of being deliquescent and highly soluble. It has been long used in medicine as a febrifuge under the name of *spirit of Mindererus*.

The *acetates of baryta, strontia, and lime*, are of little importance. The former is occasionally employed as a re-agent. The latter crystallizes in very slender acicular crystals of a silky lustre, and is chiefly employed in the preparation of the acetate of soda.

The acetate of alumina is formed by adding the acetate of lead to sulphate of alumina, when the sulphate of lead subsides and the acetate of alumina remains in solution. It is used by Dyers and Calico Printers as a basis or mordant.

*Acetate of lead*.—This salt, long known by the names of sugar of lead (*saccharum saturni*) and *cerussa acetata*, is made by dissolving either the carbonate of lead or litharge in distilled vinegar. The solution has a sweet, succeeded by an astringent taste, does not redden litmus paper, and deposits shining acicular crystals by evaporation. The crystals effloresce slowly by exposure to the air, and require about four times their weight of water at 60° F. for solution. They are composed, according to Berzelius and Thomson, of 50 parts or one atom of



the acid, 112 parts or one atom of the protoxide of lead, and 27 parts or three atoms of water.

The acetate of lead is partially decomposed, with formation of the carbonate of lead, by water which contains carbonic acid, or by exposure to the air; but a slight addition of acetic acid renders the solution quite clear.

This salt is much used in the arts, as a sedative and astringent in medical and surgical practice, and as a re-agent in chemistry.

The *sub-acetate* of lead, commonly called *extractum saturni*, is prepared by boiling one part of the neutral acetate, and two parts of litharge, deprived of carbonic acid by heat, with 25 parts of water.

This salt is less sweet and less soluble in water than the neutral acetate, has an alkaline re-action, and crystallizes in white plates by evaporation. It is decomposed by a current of carbonic acid, with production of pure carbonate of lead; and forms a turbid solution, owing to the formation of a carbonate, when it is mixed with water in which carbonic acid is present. It appears from the analysis of Berzelius to consist of one atom of acid and three atoms of the oxide of lead, and is therefore a *tris-acetate*.

A *di-acetate* may likewise be formed by boiling with water a mixture of litharge and acetate of lead in atomic proportion. (Thomson.)

*Acetate of copper*.—The pigment, called *verdigris*, which is an impure acetate of the peroxide of copper, may be formed by exposing metallic copper to the vapour of vinegar, when the metal gradually absorbs oxygen from the atmosphere, and then unites with the acid. It is prepared in large quantity in the south of France by covering copper plates with the refuse of the grape after the juice has been extracted for making wine. The saccharine matter contained in the husks furnishes acetic acid by fermentation, and in four or six weeks the plates acquire a coating of the acetate.

Verdigris is commonly of a pale green, but sometimes of a blue colour. Its essential constituent is an acetate of copper, composed, according to Mr Phillips\*, of 80 parts or one atom of the peroxide of copper, 50 parts or one atom of acetic acid, and six atoms of water. This compound is decomposed by water, and is converted into an insoluble green *di-acetate*, and into a soluble *bin-acetate* of copper. The first, as its name implies, consists of one atom of acid and two atoms of the oxide. The bin-acetate crystallizes readily in rhombic octahedrons of a green colour, and is soluble in twenty times its weight of cold, and in five of boiling water. It is conveniently prepared by dissolving verdigris in distilled vinegar, and evaporating the solution. The crystals consist of one atom of acid and two atoms of the peroxide of copper, combined, according to Mr Phillips, with three, and according to Berzelius and Dr Ure, with two atoms of water.

Besides these compounds, Berzelius has described three other acetates of copper; but as they are of little importance, I refer the reader to the original paper on the subject. (Annals of Philosophy, N. S. vol. viii.)

*Acetate of zinc*.—This salt may be prepared by way of double decomposition by mixing one atom of the sulphate of zinc, dissolved in water, with one atom of the acetate of lead. When made in this way

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\* Annals of Philosophy, N. S. vol. i. ii. and iv.

it is very apt to retain some sulphate of lead in solution. The best mode of obtaining it quite pure, is by suspending metallic zinc in a dilute solution of the acetate of lead, until all the lead is removed. (Page 292.) This is known to be accomplished by the addition of sulphuretted hydrogen, which then occasions a pure white precipitate. This salt is frequently employed as an astringent collyrium.

*Acetate of mercury.*—The only interesting compound of mercury and acetic acid is the acetate of the protoxide, which is sometimes employed in the practice of medicine. It is prepared by mixing one atom of the crystallized protonitrate of mercury with one atom of the neutral acetate of potassa. (See the table of atomic weights.) If both salts are dissolved in a considerable quantity of hot water, the solutions retain their transparency after being mixed; but on cooling, the protoacetate of mercury is deposited in white scales of a silky lustre. It is easily decomposed; and it should be dried by a very gentle heat, and washed with cold water slightly acidulated with acetic acid.

### *Oxalic Acid.*

The oxalic acid exists ready formed in several plants, especially in the *rumex acetosa* or common sorrel, and in the *oxalis acetosella* or wood sorrel; but it almost always occurs in combination either with lime or potassa. These plants contain the binoxalate of potassa; and the oxalate of lime has been found in large quantity by M. Braconnot in several species of lichen.

Oxalic acid is easily made artificially by digesting sugar in five or six times its weight of nitric acid, and expelling the excess of that acid by distillation, until a fluid of the consistence of syrup remains in the retort. The residue in cooling yields crystals of oxalic acid, the weight of which amounts to rather more than half the quantity of the sugar employed. They should be purified by solution in pure water, and recrystallization. In this process, changes of a very complicated nature ensue, during which a portion of nitric acid is resolved, chiefly, into oxygen and the deutoxide of nitrogen, while the sugar is converted, with formation of carbonic acid and water, into oxalic acid. A small quantity of malic and acetic acids are generated at the same time. As oxalic acid contains no hydrogen and less carbon than sugar, there can be no doubt that the production of this acid essentially depends upon the sugar being deprived of all its hydrogen and a portion of its carbon by oxygen derived from the nitric acid.

Many organic substances besides sugar, such as starch, gum, most of the vegetable acids, wool, hair, and silk, are converted into the oxalic by the action of nitric acid;—a circumstance which is explicable on the fact that the oxalic acid contains more oxygen than every other principle, whether of animal or vegetable origin.

Oxalic acid crystallizes in slender, flattened, quadrilateral prisms terminated by two-sided summits; but their primary form is an oblique rhombic prism. It has an exceedingly sour taste, reddens litmus paper strongly, and forms neutral salts with alkalis. The crystals effloresce on exposure to the air, but undergo no other change. They are soluble in twice their weight of cold and in their own weight of boiling water. They are dissolved also by alcohol, though less freely than in water. They contain half their weight of water of crystallization, a part of which only, amounting to about 28 per cent., can be expelled by heat without decomposing the acid itself.

The atomic weight of oxalic acid, as determined by Dr Thomson, is precisely 36; and the crystals consist of 36 parts or one atom of real acid, and 36 parts or four atoms of water. (First Principles, vol. ii.) It differs in composition from all other vegetable acids in containing no hydrogen, the absence of which seems fully established by the analyses of Berzelius, Thomson, and Ure. From the researches of these chemists, oxalic acid is composed of one part of carbon and two parts of oxygen; and since its atomic weight is 36, it must be regarded as a compound of

Carbon	.	12	.	or 2 atoms
Oxygen	.	24	.	or 3 atoms.
		<hr/>		
		36		

It is therefore intermediate between carbonic oxide and carbonic acid, and may even be supposed to consist of

Carbonic oxide	.	14 or one atom
Carbonic acid	.	22 or one atom.
		<hr/>
		36

Consistently with this view, Döbereiner found that oxalic acid is converted into carbonic acid and carbonic oxide by the action of a very large excess of fuming sulphuric acid. (An. de Ch. et de Ph. vol. xix.)

Oxalic acid is one of the most powerful and rapidly fatal poisons which we possess; and frequent accidents have occurred from its being solid and taken by mistake for Epsom salts, with the appearance of which its crystals have some resemblance. These substances may be easily distinguished, however, by the strong acidity of oxalic acid, which may be tasted without danger, while the sulphate of magnesia is quite neutral, and has a bitter saline taste. The experiments of Drs Christison and Coindet have demonstrated that chalk and magnesia are certain antidotes to poisoning by oxalic acid, in consequence of forming with it insoluble and inert compounds. (Edinburgh Medical and Surgical Journal for 1823.)

Oxalic acid is easily distinguished from all other acids by the form of its crystals, and by its solution giving with lime water a white precipitate, which is insoluble in an excess of the acid.

The salts of oxalic acid are termed *oxalates*. Most of these compounds are either insoluble or sparingly soluble in water; but they are all dissolved by the nitric, and also by the muriatic acid, except when the latter precipitates the base of the salts. The only oxalates which are remarkable for solubility are those of potassa, soda, lithia, ammonia, alumina, and iron.

A soluble oxalate is easily detected by adding to its solution a neutral salt of lime or lead, when a white oxalate of those bases will be thrown down. On digesting the precipitate in a little sulphuric acid, an insoluble sulphate is formed, and the solution yields crystals of oxalic acid on cooling. All insoluble oxalates, the bases of which form insoluble compounds with sulphuric acid, may be decomposed in a similar manner. All other insoluble oxalates may be decomposed by potassa, by which means a soluble oxalate is procured.

The oxalates, like all salts which contain a vegetable acid, are decomposed by a red heat, a carbonate being left, provided the oxide can

retain carbonic acid at a temperature which is employed. As the oxalic acid is so highly oxidized, its salts leave no charcoal when heated in close vessels.

Several oxalates are reduced to the metallic state, with evolution of pure carbonic acid, when heated to redness in close vessels. (Page 283.) The peculiar constitution of oxalic acid accounts for this change; for one atom of the acid requires precisely one atom of oxygen, which is the exact quantity contained in the oxide of a neutral oxalate of a protoxide, for being converted into carbonic acid.

*Oxalates of Potassa.*—Oxalic acid forms with potassa three compounds, of which the description was given, and the composition determined, in the year 1808 by Dr Wollaston. (Philos. Trans. for 1808.) The first is the neutral oxalate which is formed by neutralizing carbonate of potassa with oxalic acid. It crystallizes in oblique quadrangular prisms, which have a cooling bitter taste, require about twice their weight of water at 60° F. for solution, and contain 36 parts or one atom of oxalic acid, 48 parts or one atom of potassa, and one atom of water. This salt is much employed as a re-agent for detecting lime. The binoxalate of potassa is contained in sorrel, and may be procured from that plant by solution and crystallization. It crystallizes readily in small rhomboids, which are less soluble in water than the neutral oxalate. It is often sold under the name of *essential salt of lemons* for removing iron moulds from linen;—an effect which it produces by one atom of its acid uniting with the oxide of iron and forming a soluble oxalate. The third salt contains twice as much acid as the preceding compound, and has hence received the name of *quadroxalate* of potassa. It is the least soluble of these salts, and is formed by digesting the binoxalate in nitric acid, by which it is deprived of one-half of its base. It is composed of four atoms of acid, one atom of potassa, and seven of water.

The *oxalate of soda*, which may be made in the same manner as the oxalate of potassa, is very rarely employed, and is of little importance. It likewise forms a binoxalate, but no quadroxalate is known.

The oxalate of ammonia, prepared by neutralizing that alkali with oxalic acid, is much used as a re-agent. It is very soluble in hot water, and is deposited in acicular crystals when a saturated hot solution is allowed to cool. The crystals contain two atoms of water. Dr Thomson has likewise described a binoxalate of ammonia, which is less soluble than the preceding and contains three atoms of water.

*Oxalate of Lime.*—This salt, like all the insoluble oxalates, is easily prepared by the way of double decomposition. It is a white finely divided powder, which is remarkable for its extreme insolubility in pure water. On this account a soluble oxalate is an exceedingly delicate test for lime. It is very soluble, however, in muriatic and nitric acids. It is composed of 36 or one atom of the acid, and 28 parts or one atom of lime. It may be exposed to a temperature of 560° F. without decomposition, and is then quite anhydrous. No binoxalate of lime is known.

This salt is interesting in a pathological point of view, because urinary concretions are not unfrequently composed of it. It is the basis of what is called the *mulberry calculus*.

*Oxalate of Magnesia.*—This salt may be prepared by mixing oxalate of ammonia with a hot concentrated solution of the sulphate of magnesia. It is a white powder, which is very sparingly soluble in water; but, nevertheless, when the sulphate of magnesia is moderately

diluted with cold water, the oxalate of ammonia occasions no precipitate. On this fact is founded the best analytic process for separating lime from magnesia.

### Tartaric Acid.

This acid exists in the juice of several acidulous fruits, but it is almost always in combination with lime or potassa. It is prepared by mixing intimately 198 parts or one atom of cream of tartar, in fine powder, with 50 parts or one atom of chalk, and throwing the mixture by small portions at a time into ten times its weight of boiling water. On each addition, a brisk effervescence ensues, owing to the escape of carbonic acid, and one atom of the insoluble tartrate of lime subsides, while one atom of the neutral tartrate of potassa is held in solution. On washing the former with water, and then digesting it, diffused through a moderate portion of water, with one atom of sulphuric acid, the tartaric acid is set free, and after being separated from the sulphate of lime by a filter, may be procured in crystals by evaporation.

Tartaric acid has a sour taste, which is very agreeable when diluted with water. It reddens litmus paper strongly, and forms with alkalies neutral salts, to which the name of *tartrates* is applied. It requires five or six times its weight of water at 60° for solution, and is much more soluble in boiling water. It is dissolved likewise, though less freely, in alcohol. The aqueous solution is gradually decomposed by keeping, and a similar change is experienced under the same circumstances by most of the tartrates. The crystals may be exposed to the air without change. They are converted into the oxalic by digestion in nitric acid. When heated in close vessels, it fuses, froths up, and is decomposed, yielding, in addition to the usual products of destructive distillation, a distinct acid, to which the name of *pyro-tartaric acid* is applied. A considerable quantity of charcoal remains.

The atomic weight of tartaric acid, inferred by Dr Thomson from the tartrates of potassa and lead, is 66; and the crystals, which cannot be deprived of their water by heat without decomposition, consist of 66 parts or one atom of acid, and one atom of water. According to the analysis of Dr Prout and Dr Thomson, which agrees pretty closely with that of Berzelius, the acid itself is composed of

Carbon	.	24	.	or 4 atoms
Oxygen	.	40	.	or 5 atoms
Hydrogen	.	2	.	or 2 atoms.
<hr/>				
66				

Tartaric acid is distinguished from other acids by forming a white precipitate, the bitartrate of potassa, when mixed with any of the salts of that alkali. This acid, therefore, separates potassa from every other acid. It occasions a white precipitate with lime water, which is very soluble in an excess of the acid.

The tartaric acid is remarkable for its tendency to form double salts, the properties of which are often more interesting than the simple salts. The most important of these double salts, and the only ones which have been much studied, are the tartrate of potassa and soda, and the tartrate of antimony and potassa. The neutral tartrates of the alkalies, of magnesia and copper, are soluble in water; but most of the tartrates of the other bases, and especially those of lime, baryta, stron-



tia, and lead, are insoluble. All these neutral tartrates, however, which are insoluble in pure water, are soluble in an excess of their acid. They are decomposed by digestion in carbonate of potassa, and when an acid is added in excess, the bitartrate of potassa is precipitated. All the insoluble tartrates are easily procured from the neutral tartrate of potassa by way of double decomposition.

*Tartrates of potassa.*—The neutral tartrate, frequently called *soluble tartar*, is formed by neutralizing a solution of the bitartrate with carbonate of potassa; and is a product of the operation above described for making tartaric acid. It crystallizes in large four-sided prisms, which are very soluble in water, and attract moisture when exposed to the air. The crystals consist of 114 parts or one atom of the neutral tartrate and two atoms of water. They are rendered quite anhydrous by a temperature not exceeding 248° Fahr.

Of the *bitartrate*, an impure form, commonly known by the name of *tartar*, is found encrusted on the sides and bottom of wine casks, a source from which all the tartar of commerce is derived. This salt exists in the juice of the grape, and, owing to its insolubility in alcohol, is gradually deposited during the vinous fermentation. In its crude state it is coloured by the wine from which it was procured; but when purified, is quite white, and in this state constitutes the *cream of tartar* of the shops.

The bitartrate of potassa is very sparingly soluble in water, requiring sixty parts of cold and fourteen of boiling water for solution, and is deposited from the latter in cooling in small crystalline grains. It has a sour taste, and distinct acid re-action. It consists of one atom of potassa, and two atoms of the acid, united, according to Berzelius, with one atom, and according to Dr Thomson, with two atoms of water. Assuming the latter to be correct, the atomic weight of the bitartrate is 198. Its water of crystallization cannot be expelled without decomposing the salt itself.

The bitartrate of potassa is employed in the formation of tartaric acid and all the tartrates. It is likewise used in preparing pure carbonate of potassa. When exposed to a strong heat, it yields an acid empyreumatic oil, some pyro-tartaric acid, together with water, carburetted hydrogen, carbonic oxide, and carbonic acid gases, the last of which combines with the potassa. The fixed products are carbonate of potassa and charcoal, which may be separated from each other by solution and filtration. When deflagrated with half its weight of nitre, by which a part of the charcoal is consumed, it forms *black-flux*; and when an equal weight of nitre is used, so as to oxidize all the free carbon of the tartaric acid, a pure carbonate of potassa, called *white-flux*, is procured.

*Tartrate of potassa and soda.*—This double salt, which has been long employed in medicine under the name of *seignette* or *rochelle salt*, is prepared by neutralizing the bitartrate of potassa with carbonate of soda. By evaporation it forms prismatic crystals, which are soluble in five parts of cold and in a less quantity of boiling water, and are composed of 114 parts or one atom of the tartrate of potassa, 98 parts or one atom of the tartrate of soda, and eight atoms of water. The *tartrate of soda* is of little importance. It is frequently made extemporaneously by dissolving equal weights of tartaric acid and the bicarbonate of soda in separate portions of water, and then mixing the solution. A very agreeable effervescing draught is procured in this

way. Soda is better adapted for this purpose than potassa, because the former has little or no tendency to form an insoluble bitartrate.

*Tartrate of antimony and potassa.*—This compound, long celebrated as a medicinal preparation under the name of *tartar emetic*, is made by boiling the protoxide of antimony with a solution of the bitartrate of potassa. The oxide of antimony is furnished for this purpose in various ways. Sometimes the *glass* or *crocus* of that metal is employed. The Edinburgh college prepare an oxide by deflagrating the sulphuret of antimony with an equal weight of nitre; and the college of Dublin employ the submuriate. Mr Phillips recommends that 100 parts of metallic antimony in fine powder should be boiled to dryness in an iron vessel, with 200 parts of sulphuric acid, and that the residual sub-sulphate be boiled with an equal weight of cream of tartar. The solution of the double salt, however made, should be concentrated by evaporation, and allowed to cool in order that crystals may form.

The tartrate of antimony and potassa commonly crystallizes in tetrahedrons, which are often transparent when first formed, but become white and opaque by exposure to the air. It has a styptic metallic taste, reddens litmus paper slightly, and is soluble in fifteen parts of water at 60°, and in three of boiling water. (Dr Duncan, jun.) Its aqueous solution, like that of all the tartrates, undergoes spontaneous decomposition by keeping; and therefore, if kept in the liquid form, alcohol should be added in order to preserve it. According to the analysis of Dr Thomson, (First Principles, vol. ii. p. 441) it is composed of

Tartaric acid	.	(66 × 2)	.	132 or 2 atoms
Protoxide of Antimony	.	(52 × 3)	.	156 or 3 atoms
Potassa	.	.	.	48 or 1 atom
Water	.	.	.	18 or 2 atoms.

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With this result, the analysis of Mr Phillips accords, except that he found three instead of two atoms of water. The atomic weight of the salt would, on this estimate, be 363.

Tartar emetic is decomposed by many reagents. Thus alkaline substances, from their superior attraction for tartaric acid, separate the oxide of antimony. The pure alkalies, indeed, and especially potassa and soda, precipitate it imperfectly, owing to their tendency to unite with and dissolve the oxide; but the alkaline carbonates throw down the oxide much more completely. Lime water occasions a white precipitate, which is a mixture of the oxide or tartrate of antimony and tartrate of lime. The stronger acids, such as the sulphuric, nitric, and muriatic, cause a white precipitate, consisting of the bitartrate of potassa and a sub-salt of antimony. Decomposition is likewise effected by several metallic salts, the bases of which yield insoluble compounds with tartaric acid. Sulphuretted hydrogen throws down the orange sulphuret of antimony. It is precipitated by many vegetable substances, especially by an infusion of gall-nuts, and other similar astringent solutions, with which it forms a dirty white precipitate, which is regarded as a compound of tannin and the oxide of antimony. This combination is inert, and therefore a decoction of cinchona bark is recommended as an antidote to tartar emetic.

## Citric Acid.

This acid is contained in many of the acidulous fruits, but exists in large quantity in the juice of the lime and lemon, from which it is procured by a process very similar to that described for preparing tartaric acid. To any quantity of lime or lemon juice, finely powdered chalk is added as long as effervescence ensues; and the insoluble citrate of lime, after being well washed with water, is decomposed by digestion in dilute sulphuric acid. The insoluble sulphate of lime is separated by a filter, and the citric acid obtained in crystals by evaporation. They are rendered quite pure by being dissolved in water and re-crystallized. The proportions required in this process are 86 parts or one atom of the dry citrate of lime, and 49 parts or one atom of strong sulphuric acid, which should be diluted with about ten parts of water.

Citric acid crystallizes in rhomboidal prisms terminated by four plain surfaces. The crystals are large and transparent, undergo no change in the air, and if kept dry may be preserved for any length of time without decomposition. They have an intensely sour taste, redden litmus paper, and neutralize alkalies. Their flavour when diluted is very agreeable. They are soluble in an equal weight of cold and in half their weight of boiling water, and are also dissolved by alcohol. The aqueous solution is gradually decomposed by keeping. It is converted into the oxalic by the action of nitric acid. Exposed to heat, the crystals undergo the watery fusion, and the acid itself is decomposed before all its water of crystallization is expelled. Besides the usual products of the decomposition of vegetable matter, a peculiar acid sublimes, to which the name of *pyro-citric acid* is applied.

The atomic weight of citric acid, as deduced from the composition of the citrate of lead by Thomson and Berzelius, is 58; and the crystals consist of 58 parts or one atom of the acid, and 18 parts or two atoms of water. According to the analyses of the same chemists, this acid is inferred to consist of

Carbon	.	24	.	or 4 atoms
Oxygen	.	32	.	or 4 atoms
Hydrogen	.	2	.	or 2 atoms.
		—		
		58		

The analyses of Gay-Lussac and Thénard, and of Dr Ure\*, would lead to a different statement; but the foregoing agrees better with the atomic weight of the acid.

Citric acid is characterized by its flavour, by the form of its crystals, and by forming an insoluble salt with lime and a deliquescent soluble compound with potassa. It does not render lime water turbid, unless the latter is in excess, and fully saturated with lime in the cold.

Citric acid is chiefly employed as a substitute for lemon juice. On some occasions, as in making effervescing draughts or acidulous drinks, tartaric acid may be used with equal advantage.

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\* Philosophical Transactions for 1822.

The salts of citric acid are of little importance. The citrates of potassa, soda, ammonia, magnesia, and iron, are soluble in water. The first is often made extemporaneously as an effervescing draught. The citrates of lime, baryta, and strontia, lead, mercury, and silver, are very sparingly soluble. All of them are dissolved by an excess of their own acids, and are decomposed by sulphuric acid.

### *Malic Acid.*

This acid is contained in most of the acidulous fruits, being frequently associated with the tartaric and citric acids. Grapes, currants, gooseberries, and oranges, contain it. Vauquelin found it in the tamarind mixed with the tartaric and citric acids, and in the house leek, (*sempervivum tectorum*,) combined with lime. It is contained in considerable quantity in apples, a circumstance to which it owes its name. It is almost the sole acidifying principle of the berries of the service tree, (*sorbus aucuparia*,) in which it was detected by Mr Donovan, and described by him under the name of *sorbic acid* in the Philosophical Transactions for 1815; but it was afterwards identified with the malic acid by Braconnot and Houton-Labillardière. (An. de Ch. et de Ph. vol. viii.)

The malic acid may be formed by digesting sugar with three times its weight of nitric acid; but the best mode of procuring it is from the berries of the service tree. The juice, previously freed as much as possible from the red colouring matter of the berry by means of charcoal, is mixed with the acetate of lead as long as a precipitate ensues. The malate of lead, after being well washed with cold water, is dissolved by boiling water, from which it is deposited on cooling in acicular crystals of a brilliant lustre. The salt is at first always coloured; but it may be made quite white by repeated solution and crystallization. It is then decomposed by a quantity of dilute sulphuric acid, insufficient for combining with all the oxide of lead, when a solution is procured which contains malic acid together with a little lead. The latter is afterwards precipitated by sulphuretted hydrogen.

Malic acid has a very pleasant acid taste. It crystallizes with great difficulty and in an imperfect manner, attracts moisture from the atmosphere, and is very soluble in water and alcohol. Its aqueous solution is gradually decomposed by keeping. Nitric acid converts it into the oxalic acid. Heated in close vessels it is decomposed with formation of a new and volatile acid, which has hence received the name of *pyro-malic acid*.

The composition of malic acid has not been satisfactorily determined. The only analysis of it is by M. Vauquelin, who found so large a quantity of hydrogen comparatively with the oxygen, that the accuracy of his result may fairly be questioned.

Most of the salts of the malic acid are more or less soluble in water. The malates of soda and potassa are deliquescent and very soluble. Those of lead and lime, the most insoluble of the malates, are sparingly soluble in cold water, but are freely dissolved by that liquid at a boiling temperature, a circumstance which distinguishes the malic from the oxalic, tartaric, and citric acids.

### *Benzoic Acid.*

Benzoic acid exists in gum benzoin, in storax, in the balsams of

Peru and Tolu, and in several other vegetable substances. M. Vogel has detected it in crystals between the skin and kernel of the Tonquin bean, and in the flowers of the *trifolium melilotus officinalis*. It is found in considerable quantity in the urine of the cow and other herbivorous animals, and is perhaps derived from the grasses on which they feed. It has also been detected in the urine of children.

This acid is commonly extracted from gum benzoin. One method consists in heating the benzoin in an earthen pot, over which is placed a cone of paper to receive the acid as it sublimes; but since the product is always impure, owing to the presence of empyreumatic oil, it is better to extract the acid by means of an alkali. The usual process consists in boiling finely powdered gum benzoin in a large quantity of water along with lime or the carbonate of potassa, by which means a benzoate is formed. To the solution, after being filtered and concentrated by evaporation, muriatic acid is added, which unites with the base, and throws down the benzoic acid. It is then dried by a gentle heat, and purified by sublimation.

Benzoic acid has a sweet and aromatic rather than a sour taste; but it reddens litmus paper, and neutralizes alkalies. It fuses readily by heat, and at a temperature a little above its point of fusion, it is converted into vapour, emitting a peculiar, fragrant, and highly characteristic odour, and condensing on cool surfaces without change. When strongly heated, it takes fire, and burns with a clear yellow flame. It undergoes no change by exposure to the air, and is not decomposed by the action even of nitric acid. It requires about 24 parts of boiling water for solution, and nearly the whole of it is deposited on cooling in the form of minute acicular crystals of a silky lustre. It is very soluble in alcohol, especially by the aid of heat.

Benzoic acid is easily distinguished by its odour and volatility. Its salts are all decomposed by the muriatic acid, with deposition of benzoic acid if the solution is moderately concentrated.

The atomic weight of benzoic acid, as inferred from the analysis of the benzoate of lead by Berzelius, and that of the benzoate of the peroxide of iron by Dr Thomson, is 120.

The ultimate analysis of this acid by Berzelius\*, together with the number representing the weight of its atom, appears to justify the opinion that it is composed of

Carbon	.	90	.	or 15 atoms
Oxygen	.	24	.	or 3 atoms
Hydrogen	.	6	.	or 6 atoms.
<hr/>				
120				

According to the analysis of Dr Ure, it contains 13 instead of 15 atoms of carbon. (Philos. Trans. for 1822.)

Most of the benzoates are soluble in water. Those of lead, mercury, and the peroxide of iron are the most insoluble. The benzoate of soda and ammonia are sometimes employed for separating iron from manganese. If the solution is quite neutral, the peroxide of iron is completely precipitated, while the manganese remains in solution.

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\* Annals of Philosophy, vol. v.



*Gallic Acid.*

This acid was discovered by Scheele in 1786, and exists ready formed in the bark of many trees, and in gall-nuts. It is always associated with tannin, a substance to which it is allied in a manner hitherto unexplained.

Several processes have been described for the preparation of gallic acid; but the most economical appears to be that of Scheele as modified by M. Braconnot. (*An. de Ch. et de Ph.* vol. ix.) Any quantity of gall-nuts, reduced to powder, is infused for a few days in four times its weight of water; and the infusion, after being strained through linen, is kept for two months in a moderately warm atmosphere. During this period, the surface of the liquid becomes mouldy, the tannin of the gall-nuts disappears more or less completely, and a yellowish crystalline matter is deposited. On evaporating the solution to the consistence of a syrup, and allowing it to cool, an additional quantity of the same substance subsides. The gallic acid, thus procured, is impure, owing to the presence of colouring matter and a peculiar acid, to which M. Braconnot has applied the name of *ellagic acid*. The gallic acid is separated from the latter by boiling water, in which the ellagic acid is insoluble; and it is rendered white by digestion with animal charcoal deprived of its phosphate of lime by muriatic acid. When the colourless solution is concentrated by evaporation, the gallic acid is deposited in small white acicular crystals of a silky lustre.

Gallic acid has a weak sour taste, accompanied with a slight sensation of astringency. It reddens litmus paper, and effervesces with the alkaline carbonates. It is soluble in twenty-four parts of cold and in three of boiling water; and is likewise dissolved by alcohol. The aqueous solution becomes mouldy by keeping. Nitric acid converts it into the oxalic acid. When strongly heated in the open air, it takes fire. At a high temperature in close vessels it is in part decomposed, and in part sublimes, apparently without change.

The composition and atomic weight of gallic acid has not been determined in a satisfactory manner. From an analysis of the gallate of lead by Berzelius, the equivalent of the acid is probably about 63 or 64; and according to the same chemist it is composed of

Carbon	.	.	56.64
Oxygen	.	.	38.36
Hydrogen	.	.	5.00*

With lime water gallic acid yields a brownish-green precipitate, which is redissolved by an excess of the solution, and acquires a reddish tint. It is distinguished from tannin by causing no precipitate in a solution of gelatine. With a salt of iron it forms a dark blue coloured compound, which is the basis of ink. The finest colour is procured when the peroxide and protoxide of iron are mixed together. This character distinguishes gallic acid from every other substance excepting tannin.

The salts of gallic acid, called *gallates*, have been imperfectly examined. The gallates of potassa, soda, and ammonia are soluble in

water; but most of the other gallates are of sparing solubility. On this account many of the metallic solutions are precipitated by gallic acid.

### Succinic Acid.

This acid is procured by heating powdered amber in a retort by a regulated temperature, when the succinic acid passes over and condenses in the receiver. It is at present uncertain whether it exists ready formed in amber, or is a product of the destructive distillation. As first obtained, it has a yellow colour and peculiar odour, owing to the presence of some empyreumatic oil; but it is rendered quite pure and white by being dissolved in nitric acid, and then evaporated to dryness. The oil is decomposed, and the succinic acid is left unchanged.

Succinic acid has a sour taste, and reddens litmus paper. It is soluble both in water and alcohol, and crystallizes by evaporation in anhydrous prisms. When briskly heated, it fuses, undergoes decomposition, and in part sublimes, emitting a peculiar and very characteristic odour.

The salts of succinic acid have been little examined. The succinates of the alkalies are soluble in water. That of ammonia is frequently employed for separating iron from manganese, the succinate of the peroxide of iron being quite insoluble in water, provided the solutions are neutral. The succinate of manganese, on the contrary, is soluble.

The atomic weight of succinic acid, deduced from the composition of the succinate of iron and of lead by Thomson and Berzelius, is 50; and according to the analysis of the succinate of lead by Berzelius, this acid is inferred to consist of

Carbon	.	24	.	or 4 atoms
Oxygen	.	24	.	or 3 atoms
Hydrogen	.	2	.	or 2 atoms.
		—		
		50		

From this it appears that the succinic is identical with the acetic acid, both in the proportion of its constituents and in the weight of its atom. If this is true, and there seems no good reason to doubt the accuracy of the data, the sole difference between these acids consists in the manner in which their elements are combined, a circumstance which is very favourable to the opinion already mentioned relative to the constitution of organic substances in general. (Page 347.)

*Camphoric acid.*—This compound has not hitherto been found in any plant, and is procured only by digesting camphor for a considerable time in a large excess of nitric acid. It is sparingly soluble in water. Its taste is rather bitter, and its odour somewhat similar to saffron. It reddens litmus paper, and combines with alkalies, forming salts which are called *camphorates*. This acid has not been applied to any useful purpose.

The *Mucic* or *Saccholactic acid* was discovered by Scheele in 1780. It is obtained by the action of nitric acid on certain substances, such as gum, manna, and the sugar of milk. The readiest and cheapest mode of forming it, is by digesting gum with three times its weight of nitric acid. On applying heat, effervescence ensues, and three acids

—the oxalic, malic, and saccholactic, are the products. The latter, from its insolubility, subsides as a white powder, and may be separated from the others by washing with cold water.

The saccholactic is a weak acid, which is insoluble in alcohol, and requires sixty times its weight of boiling water for solution. When heated in a retort it is decomposed, and, in addition to the usual products, yields a volatile white substance, to which the name of *pyromucic acid* has been applied.

*Moroxylie acid.*—This compound, which was discovered by Klaproth, is found in combination with lime on the bark of the *morus alba* or white mulberry, and has hence received the appellation of *morie* or *moroxylie acid*. It is obtained by decomposing the moroxylate of lime by acetate of lead, and then separating the lead from the moroxylate of that base by means of sulphuric acid.

The *Hydrocyanic* or *Prussic acid*, which is not an unfrequent production of plants, has already been described.

The *Sorbic*, as already mentioned, has been shown to be the malic acid.

*Rheumic acid.*—This name was applied to the acid principle contained in the stem of the garden rhubarb; but M. Lassaigue has shown it to be the oxalic acid.

The *Boletic acid* was discovered by M. Braconnot, in the juice of the *Boletus pseudo-ignarius*. As it is a compound of no importance, I refer the reader to the original paper for an account of it. (Annals of Phil. vol. ii.)

*Igasuric acid.*—M. Pelletier and Caventou have proposed this name for the acid which occurs in combination with strychnia in the nuxvomica and St Ignatius's bean; but its existence, as different from all other known acids, is doubtful.

*Mellitic acid.*—This acid is contained in the rare substance called *honey-stone*, which is occasionally met with at Thuringia in Germany. The honey-stone, according to Klaproth, is a mellitate of alumina, and on boiling it in a large quantity of water, the acid is dissolved, and the alumina subsides. On concentrating the solution, the mellitic acid is deposited in minute acicular crystals. From its rarity it has been little studied, and is of little importance.

The *Suberic acid* is procured by the action of nitric acid on cork. Its acid properties are feeble. It is very soluble in boiling water, and the greater part of it is deposited from the solution in cooling in the form of a white powder. Its salts, which have been little examined, are known by the name of *suberates*.

*Zumic acid.*—This compound, procured by Braconnot from several vegetable substances which had undergone the acetous fermentation, appears from the observations of Vogel to be the lactic acid. (Annals of Philosophy, vol. xii.)

*Kinic acid.*—This acid exists in the cinchona bark in combination with lime. On evaporating an infusion of bark to the consistence of an extract, and treating the residue with alcohol, a viscid matter remains, consisting of the kinate of lime and mucilaginous matters. On dissolving it in water, and allowing the concentrated solution to evaporate spontaneously in a warm place, the kinate crystallizes in plates which are either cubic or rhomboidal. From a solution of this salt Vauquelin precipitated the lime by means of oxalic acid, and thus obtained kinic acid in a pure state. (An. de Ch. vol. lix.)

The kinic acid has an acid taste and reddens vegetable blue colours.

It is very soluble in water, and crystallizes with difficulty. It forms soluble compounds with the alkalies and alkaline earths, and is not precipitated by a salt of mercury, lead, or silver.

The *Meconic acid*, which is combined with morphia in opium, will be most conveniently described in the following section.

## SECTION II.

### *VEGETABLE ALKALIES.*

Under this title are comprehended those proximate vegetable principles which are possessed of alkaline properties. The honour of discovering the existence of this class of bodies is due to Sertuerner, a German apothecary, who published an account of morphia so long ago as the year 1803; but the subject excited no notice until the publication of his second essay in 1816. The chemists who have since cultivated this department with success are M. Robiquet, and MM. Pelletier and Caventou.

All the vegetable alkalies, according to the researches of Pelletier and Dumas, consist of carbon, hydrogen, oxygen, and nitrogen. (An. de Ch. et de Ph. vol. xxiv.) They are decomposed with facility by nitric acid and by heat, and ammonia is always one of the products of the destructive distillation. They never exist in an insulated state in the plants which contain them; but are apparently in every case combined with an acid, with which they form a salt more or less soluble in water. These alkalies are for the most part very insoluble in water, and of sparing solubility in cold alcohol; but they are all readily dissolved by that fluid at a boiling temperature, being deposited from the solution, commonly in the form of crystals, on cooling. Most of the salts are far more soluble in water than the alkalies themselves, and several of them are remarkable for their solubility.

As the vegetable alkalies agree in several of their leading chemical properties, the mode of preparing one of them admits of being applied with slight variation to all. The general outline of the method is as follows.—The substance containing the alkaline principle is digested, or more commonly macerated, in a large quantity of water, which dissolves the salt, the base of which is the vegetable alkali. On adding some more powerful salifiable base, such as potassa or ammonia, or boiling the solution for a few minutes with lime or pure magnesia, the vegetable alkali is separated from its acid, and being in that state insoluble in water, may be collected on a filter and washed. As thus procured, however, it is impure, retaining some of the other principles, such as the oleaginous, resinous or colouring matters with which it is associated in the plant. To purify it from these substances, it should be mixed with a little animal charcoal, and dissolved in boiling alcohol. The alcoholic solution, which is to be filtered while hot, yields the pure alkali, either on cooling or by evaporation; and if not quite colourless, it should again be subjected to the action of alcohol and animal charcoal. In order to avoid the necessity of employing a large quantity of alcohol, the following modification of the process may be adopted. The vegetable alkali, after being precipitated and collected

on a filter, is made to unite with some acid, such as the acetic, sulphuric, or muriatic, and the solution is boiled with animal charcoal until the colouring matter is removed. The alkali is then precipitated by ammonia or some other salifiable base.

### *Morphia.*

Opium contains a great diversity of different principles, among which the following may in particular be enumerated:—morphia, meconic acid, narcotine, gummy, resinous, and extractive colouring matters, lignin, fixed oil, and a small quantity of caoutchouc. On infusing opium in water, several of these principles are dissolved, and especially the meconate of morphia, together with narcotine, which is likewise rendered soluble by an acid.

One of the best processes for preparing pure morphia is that recommended by M. Robiquet. (*An. de Ch. et de Ph.* vol. v.) The concentrated infusion of a pound of opium is boiled for a quarter of an hour with about 150 grains of pure magnesia, and the grayish crystalline precipitate, which consists of the meconate of magnesia, morphia, narcotine, colouring matter, and the excess of magnesia, is collected on a filter and edulcorated with cold water. This powder is then digested at a temperature of 120° or 130° F. in dilute alcohol, which removes the narcotine and the greater part of the colouring matter. The morphia is then taken up by concentrated boiling alcohol, and is deposited in crystals on cooling. Dr Christison informs me that by this process, conducted in the laboratory of M. Robiquet, he procured three drachms and a half of morphia from half a pound of a very pure specimen of the best Turkey opium.

Dr Thomson proposes to precipitate the morphia by ammonia, and to purify it by solution in acetic acid and digestion with animal charcoal. (*Annals of Phil.* vol. xv.) This process is very convenient, but I doubt if it gives so large a product as the foregoing. The animal charcoal should be deprived of phosphate of lime by muriatic acid before being used.

Pure morphia is white, and crystallizes readily in small rectangular prisms of a brilliant lustre. It is almost wholly insoluble in cold, and to very small extent in hot water. It is soluble in strong alcohol, especially by the aid of heat. In its pure state it has scarcely any taste; but when rendered soluble by combining with an acid or by solution in alcohol, it is intensely bitter. It has an alkaline reaction, and combines with acids, forming neutral salts, which are far more soluble in water than morphia itself, and for the most part are capable of crystallizing.

Strong nitric acid decomposes morphia, forming a red solution, which by the continued action of the acid acquires a yellow colour, and is ultimately converted into oxalic acid. This circumstance was first noticed by Pelletier and Caventou; but it is not peculiar to morphia, since nitric acid has a similar effect on strychnia.

Morphia is the narcotic principle of opium. When pure, owing to its insolubility, it is almost inert; for M. Orfila gave twelve grains of it to a dog without its being followed by any sensible effect. In a state of solution, on the contrary, it acts on the animal system with great energy, Sertuerner having noticed alarming symptoms from so small a quantity as half a grain. From this it appears to follow that the effects of an overdose of a salt of morphia may be prevented by



giving a dilute solution of ammonia, or an alkaline carbonate, so as to precipitate the vegetable alkali. When carefully administered, morphia may be employed very advantageously in the practice of medicine; since, according to Magendie, it produces the soothing effect of opium, without causing the feverish excitement, heat, and headach, which so frequently accompany the employment of that drug. The best mode of exhibiting it, is in the form of the acetate of morphia, a salt which is very soluble in water, and crystallizes in divergent prisms by evaporation. The basis of Battley's sedative liquor is supposed to be the acetate of morphia. This compound, from being inodorous, and therefore less easily detected than opium, has been employed for criminal purposes, and M. Lassaigue has minutely described a method for discovering its presence. (*An. de Ch. et de Ph.* vol. xlv.)

The composition of morphia, as will appear from the following numbers, has been stated differently by different chemists. The specimen analyzed by Dr Thomson must surely have been impure.

	<i>Pelletier and Dumas.</i>	<i>Bussy.</i>	<i>Brande.</i>	<i>Thomson.</i>
Carbon .	72.02	69.0	72.0	44.71
Oxygen .	14.84	20.0	17.0	49.69
Hydrogen .	7.61	6.5	5.5	5.59
Nitrogen .	5.53	4.5	5.5	0.00
	<hr/> 100	<hr/> 100	<hr/> 100	<hr/> 100

*Meconic acid*\*.—This acid was procured by M. Robiquet from the magnesian precipitate above mentioned, after the morphia had been separated from it. The meconate of magnesia is dissolved in dilute sulphuric acid, and muriate of baryta is then added, which throws down the sulphate and meconate of that base. By acting on this precipitate with dilute sulphuric acid, the meconic acid is set free, and crystallizes when its solution is evaporated. As it retains colouring matter very obstinately, it should be purified by sublimation.

Meconic acid has a sour, followed by a bitter taste, reddens litmus paper, and is very soluble both in water and alcohol. It is characterized by giving a red colour to a salt of the peroxide of iron, and communicates an emerald green tint to the sulphate of copper. It exerts no action on the animal system.

*Narcotine*.—This substance, though not regarded as a vegetable alkali, may be conveniently noticed in connexion with morphia. It was particularly described in 1803 by Derosne, and was long known by the name of *the salt of Derosne*. Sertuerner supposed it to be the meconate of morphia; but M. Robiquet proved that it is an independent principle, and applied to it the name of *narcotine*. It is easily prepared by evaporating an aqueous infusion of opium to the consistence of an extract, and digesting it in sulphuric ether. This solvent, which does not act on the meconate of morphia, takes up all the narcotine, and deposits it in acicular crystals by evaporation.

Pure narcotine is insoluble in cold and very slightly soluble in hot water. It dissolves in oil, ether, and alcohol, the latter, though diluted, acting as a solvent for it by the aid of heat. It does not possess alkaline properties, though it is rendered soluble in water by means of an acid. Its presence in an aqueous solution of opium seems owing to a free

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\* From *μηκων papaver*.

acid, which M. Robiquet imagines to be different from the meconic. Like the vegetable alkalies, nitrogen enters into its constitution.

The unpleasant stimulating properties of opium are attributed by Magendie to the presence of narcotine, the ill effects of which, according to the experiments of the same physiologist, are in a great degree counteracted by acetic acid. These results, though they require confirmation, render it probable that the superiority assigned to the *black drop* over the common tincture of opium of the Pharmacopœia is owing to the vegetable acids which enter into its composition.

### *Cinchonia and Quinia.*

The existence of a distinct vegetable principle in cinchona bark was inferred by Dr Duncan, junior, in the year 1803, who ascribed to it the febrifuge virtues of the plant, and proposed for it the name of *cinchonin*\*. Dr Gomez of Lisbon, whose attention was directed to the subject by the researches of Dr Duncan, succeeded in procuring cinchonin in a separate state; but its alkaline nature was first discovered in 1820 by MM. Pelletier and Caventou. It has been fully established by the labours of those chemists that the febrifuge property of bark is possessed by two alkalies, the *cinchonia* or cinchonin of Dr Duncan, and quinia, both of which are combined with kinic acid. These principles, though very analogous, are distinctly different, standing in the same relation to each other as potassa and soda. The former exists in the *Cinchona condaminea*, or pale bark; the latter is present in the *C. cordifolia*, or yellow bark; and they are both contained in the *C. oblongifolia*, or red bark. They were procured by Pelletier and Caventou by a process similar to that of M. Robiquet for preparing morphia†; and slight modifications of the method have been proposed by M. Badollier and M. Voretton‡. From one pound of yellow bark M. Voretton procured 80 grains of quinia, which is nearly 1.4 per cent.

Pure cinchonia is white and crystalline, requires 2500 times its weight of boiling water for solution, and is insoluble in cold water. Its proper menstruum is boiling alcohol; but it is dissolved in small quantity by oils and ether. Its taste is bitter, though slow in being perceived, on account of its insolubility; but when the alkali is dissolved by alcohol or an acid, the bitterness is very powerful, and accompanied by the flavour of cinchona bark. Its alkaline properties are exceedingly well marked, since it neutralizes the strongest acids. The sulphate, muriate, nitrate, and acetate of cinchonia are soluble in water, and the sulphate crystallizes in four-sided prisms. The neutral tartrate, oxalate, and gallate of cinchonia, are insoluble in cold, but may be dissolved by hot water, or by alcohol.

Quinia, which was discovered by Pelletier and Caventou, does not crystallize like cinchonia when precipitated from its solutions, but it has a white, porous, and rather flocculent aspect. It is very soluble in alcohol, forming a solution which is intensely bitter, and possesses a distinct alkaline reaction. Ether likewise dissolves it, but it is almost insoluble in water. Its febrifuge virtues are more powerful than

\* Edinburgh New Dispensatory, 11th Edit. p. 299, or Nicholson's Journal for 1803.

† Ann. de Ch. et de Ph. vol. xv.

‡ Ibid. vol. xvii.

those of cinchonia, and it is now extensively employed in the practice of medicine. It is most commonly exhibited in the form of the sulphate, a salt of such activity that three grains have been known to cure an intermittent fever. This salt, which consists of 90 parts of the alkali and 10 of the acid, crystallizes in delicate white needles, having the appearance of amianthus. It is less soluble in water than the sulphate of cinchonia, but is very bitter. It dissolves readily in strong alcohol by the aid of heat, a character which affords a useful test of its purity.

The analyses of different chemists, relative to the composition of cinchonia and quinia, do not correspond better than those of morphia, as appears by the following results:—

	<i>Pelletier and Dumas.</i>		<i>Brande.</i>	
	<i>Cinchonia.</i>	<i>Quinia.</i>	<i>Cinchonia.</i>	<i>Quinia.</i>
Carbon	76.97	74.14	79.30	73.80
Oxygen	7.97	6.77	0.00	5.55
Hydrogen	6.22	8.80	7.17	7.65
Nitrogen	9.02	10.76	13.72	13.00
	<hr/> 100.18	<hr/> 100.47	<hr/> 100.19	<hr/> 100.00

The neutral gallate, tartrate, and oxalate of quinia, like the analogous salts of cinchonia, are insoluble in cold water.

From the new facts which have been ascertained relative to the constituents of bark, the action of chemical tests on a decoction of this substance is now explicable. According to the analysis of Pelletier and Caventou, the different kinds of Peruvian bark, besides the kinate of cinchonia or quinia, contain the following substances:—a greenish fatty matter; a red insoluble matter; a red soluble principle, which is a variety of tannin; a yellow colouring matter; kinate of lime; gum; starch; and lignin. It is hence apparent that a decoction of bark, owing to the tannin which it contains, may precipitate a solution of tartar emetic, of gelatine, or a salt of iron, without containing a trace of the vegetable alkali, and consequently without possessing any febrifuge virtues.

An infusion of gall-nuts, on the contrary, causes a precipitate only by its gallic acid uniting with cinchonia or quinia, and therefore affords a test for distinguishing a good from an inert variety of bark.

### *Strychnia.*—*Brucia.*

*Strychnia.*—Strychnia was discovered in 1818 by Pelletier and Caventou in the fruit of the *Strychnos ignatia* and *Strychnos nux vomica*, and has since been extracted by the same chemists from the Upas. (An. de Ch. et de Ph. vol. x. and xxvi.) This alkali, which is prepared by processes analogous to those already described, is very soluble in boiling alcohol, and is procured in minute four-sided prisms by allowing the solution to evaporate spontaneously. It is almost insoluble in water, requiring more than 6000 parts of cold and 2500 of boiling water for solution; but notwithstanding its sparing solubility, it excites an insupportable bitterness in the mouth.—Water containing only 1-600,000th of its weight of strychnia has a bitter taste. It has a distinct alkaline reaction, and neutralizes acids, forming salts, most of which are soluble in water. It is united in the *nux vomica* and St

Ignatius's bean with the igasuric acid. (Page 365.) By the action of strong nitric acid it yields a red colour; but it appears probable, from some recent observations of Pelletier and Caventou, that the red tint is owing to the presence of some impurity.

Strychnia is one of the most virulent poisons hitherto discovered, and is the poisonous principle of the substances in which it is contained. Its energy is so great, that half a grain blown into the throat of a rabbit occasioned death in the course of five minutes. Its operation is always accompanied with symptoms of locked jaw and other tetanic affections.

Strychnia, according to the analysis of Pelletier and Dumas, is composed of 78.22 of carbon, 6.38 of oxygen, 6.54 of hydrogen, and 8.92 of nitrogen.

*Brucia*.—This alkali was discovered in the *Brucea antidysenterica* by Pelletier and Caventou soon after their discovery of strychnia; (An. de Ch. et de Ph. vol. xii.) and it likewise exists in small quantity in the St Ignatius's bean and the *nux vomica*. In its bitter taste and poisonous qualities, it is very similar to strychnia, but is twelve or sixteen times less energetic than that alkali. It is soluble both in hot and cold alcohol, especially in the former; and it crystallizes when its solution is evaporated. It is more soluble in water than most of the other vegetable alkalies, requiring only 850 times its weight of cold, and 500 of boiling water for solution. It is composed of 75.04 of carbon, 11.21 of oxygen; 6.52 of hydrogen, and 7.22 of nitrogen.

### *Veratria, Emetia, Picrotoxia, Solania, Delphia, &c.*

*Veratria*.—The medicinal properties of the seeds of the *Veratrum sa' adilla*, and of the root of the *Veratrum album* or white hellebore, and of the *Colchicum autumnale* or meadow saffron, are owing to the peculiar alkaline principle *veratria*, which was discovered by Pelletier and Caventou in 1819, and may be extracted by the usual process. (Journal de Pharmacie, vol. vi.) This alkali, which appears to exist in those plants in combination with gallic acid, is white and pulverulent, inodorous, and of an acrid taste. It requires 1000 times its weight of boiling, and still more of cold water for solution. It is very soluble in alcohol, and may also be dissolved, though less readily, by means of ether. It has an alkaline reaction, and neutralizes acids; but it is a weaker base than morphia, quinia, or strychnia. It acts with singular energy on the membrane of the nose, exciting violent sneezings though in very minute quantity. When taken internally in very small doses, it produces excessive irritation of the mucous coat of the stomach and intestines; and a few grains were found to be fatal to the lower animals.

*Veratria*, according to the analysis of Pelletier and Dumas, consists of 66.75 of carbon, 19.6 of oxygen, 8.54 of hydrogen, and 5.04 of nitrogen.

*Emetia*.—Ipecacuanha consists of an oily matter, gum, starch, lignin, and a peculiar principle, which was discovered in 1817 by M. Pelletier, and to which he has applied the name of *emetine*. (Journal de Pharmacie, vol. iii.) This substance, of which ipecacuanha contains 16 per cent. appears to be the sole cause of the emetic properties of that root, and is procured by a process similar to that for preparing the other vegetable alkalies.

*Emetia* is a white pulverulent substance, of a rather bitter and disa-

greeable taste, sparingly soluble in cold but more freely in hot water, and insoluble in ether. It is readily dissolved by alcohol. At 122 it fuses. It has a distinct alkaline reaction, and neutralizes acids; but its salts are little disposed to crystallize. (An. de Ch. et de Ph. vol. xxiv. p. 181.) According to Pelletier and Dumas, it consists of carbon 64.57, oxygen 22.95, hydrogen 7.77, and nitrogen 4.

*Picrotoxia*.—The bitter poisonous principle of the *Cocculus indicus* was discovered in 1819 by M. Boullay, who gave it the name of *picrotoxine*. Its claim to the title of a vegetable alkali, among which class of bodies it was placed by its discoverer, has been called in question by M. Casaseca, from whose remarks it seems that picrotoxia has no alkaline reaction, and does not neutralize acidity. It combines, however, with acids, and with the acetic and nitric acids forms crystallizable compounds. It appears, also, that the menispermic acid, supposed by M. Boullay to be united in the *cocculus indicus* with picrotoxia, is merely a mixture of the sulphuric and malic acids. (Edinburgh Journal of Science, No. x.)

*Solanina*.—The active principle of the *Solanum dulcamara*, or woody nightshade, was procured in a pure state by Desfosses. This compound has distinct alkaline properties, and is combined in the plant with malic acid. (Journal de Pharmacie, vol. vi. and vii.)

*Delphinia*.—This substance was discovered in the *Delphinium physagria* or *stavesacre*, by MM. Feneuille and Lassaigue. It possesses the general characters of the vegetable alkalies. (An. de Ch. et de Ph. vol. xii.)

Besides the vegetable alkalies, already described, it has been rendered highly probable, chiefly by the researches of M. Brande, that several other plants, such as the *Atropa belladonna*, *Conium maculatum*, *Hyoscyamus niger*, *Datura stramonium*, and *Digitalis*, owe their activity to the presence of an alkali.

## SECTION III.

### SUBSTANCES WHICH, IN RELATION TO OXYGEN, CONTAIN AN EXCESS OF HYDROGEN.

#### Oils.

Oils are characterized by a peculiar unctuous feel, by inflammability, and by insolubility in water. They are divided into the fixed and volatile oils, the former of which are comparatively fixed in the fire, and therefore give a permanently greasy stain to paper; while the latter, owing to their volatility, produce a stain which disappears by gentle heat.

*Fixed oils*.—The fixed oils are usually contained in the seeds of plants, as for example in the almond, linseed, rapeseed, and poppy seed; but olive oil is extracted from the pulp which surrounds the stone. They are procured by bruising the seed, and subjecting the pulpy matter to pressure in hempen bags, a gentle heat being generally employed at the same time to render the oil more limpid.

Fixed oils, the palm oil excepted, are fluid at common temperatures,



are nearly inodorous, and have little taste. They are lighter than water, their density in general varying from 0.9 to 0.96. They are commonly of a yellow colour, but may be rendered nearly or quite colourless by the action of animal charcoal. At or near the temperature of 600° F. they begin to boil, but suffer partial decomposition at the same time, an inflammable vapour being disengaged even below 500°. When heated to redness in close vessels a large quantity of the combustible compounds of carbon and hydrogen are formed, together with the other products of the destructive distillation of vegetable substances; and in the open air they burn with a clear white light, and formation of water and carbonic acid. They may hence be employed for the purposes of artificial illumination, as well in lamps, as for the manufacture of gas.

Fixed oils undergo considerable change by exposure to the air. The rancidity which then takes place is occasioned by the mucilaginous matters which they contain becoming acid. From the operation of the same cause, they gradually lose their limpidity, and some of them, which are hence called *drying* oils, become so dry that they no longer feel unctuous to the touch nor give a stain to paper. This property, for which linseed oil is remarkable, may be communicated quickly by heating the oil in an open vessel. The drying oils are employed for making oil paint, and mixed with lamp-black constitute printer's ink. During the process of drying, oxygen is absorbed in considerable quantity.

The absorption of oxygen by fixed, and especially by drying oils, is under some circumstances so abundant and rapid, and accompanied with such a free disengagement of caloric, that light porous combustible materials, such as lamp-black, hemp, or cotton-wool, may be kindled by it. Substances of this kind, moistened with linseed-oil, have been known to take fire during the space of 24 hours, a circumstance which has repeatedly been the cause of extensive fires in warehouses and in cotton manufactories.

Fixed oils do not unite with water, but they may be permanently suspended in that fluid by means of mucilage or sugar, so as to constitute an *emulsion*. They are for the most part very sparingly soluble in alcohol and ether. Strong sulphuric acid thickens the fixed oils, and forms with them a tenacious matter like soap; and they are likewise rendered thick and viscid by the action of chlorine. Concentrated nitric acid acts upon them with great energy, giving rise in some instances to the production of flame.

Fixed oils unite with the common metallic oxides. Of these compounds, the most interesting is that with the oxide of lead. When linseed oil is heated with a small quantity of litharge, a liquid results which is powerfully drying, and is employed as oil varnish. Olive oil combined with half its weight of litharge forms the common diachylon plaster.

The fixed oils are readily attacked by alkalies. With ammonia, oil forms a soapy liquid to which the name of *volatile liniment* is applied. The fixed alkalies, boiled with oil or fat, give rise to the soap employed for washing, the soft inferior kind being made with potassa, and the hard with soda. The chemical nature of soap has of late years been elucidated by the labours of M. Chevreul. This chemist has found that fixed oils and fats are not pure proximate principles, but consist of two substances, one of which is solid at common temperatures, while the other is fluid.

To the former he has applied the name of stearine from *στέας* suet, and to the latter *elaine* from *ελαιον* oil. Stearine is the chief ingredient of suet, butter, and lard, and is the cause of their solidity; whereas oils contain a greater proportional quantity of *elaine*, and are consequently fluid. These principles may be separated from one another by exposing fixed oil to a low temperature, and pressing it, when congealed, between folds of bibulous paper. The stearine is thus obtained in a separate form; and by pressing the bibulous paper under water, an oily matter is procured, which is *elaine* in a state of purity. This principle is peculiarly fitted for greasing the wheels of watches, or other delicate machinery, since it does not thicken or become rancid by exposure to the air, and requires a cold of about 20° F. for congelation. In the formation of soap the stearine and *elaine* disappeared entirely, being converted by a change in the arrangement of their elements into three compounds, to which M. Chevreul\* has applied the names of *margaric* and *oleic* acids, and *glycerine*. The two acids enter into combination with the alkali employed, and the resulting compound is soap. A similar change appears to be effected by the action not only of the alkaline earths, but of several of the metallic oxides.

Soap is decomposed by acids, and by earthy and most metallic salts. On mixing muriate of lime with a solution of soap, a muriate of the alkali is produced, and the lime forms an insoluble compound with the *margaric* and *oleic* acids. A similar change ensues when a salt of lead is employed.

According to the analysis of Gay-Lussac and Thénard, 100 parts of olive oil consist of carbon 77.213, oxygen 9.427, and hydrogen 13.36. From these proportions it is inferred that olive oil contains ten atoms of carbon, one of oxygen, and eleven of hydrogen.

*Volatile oil.*—Aromatic plants owe their flavour to the presence of a *volatile* or *essential* oil, which may be obtained by distillation, water being put into the still along with the plant, in order to prevent the latter from being burned. The oil and water pass over into the recipient, and the oil collects at the bottom or the surface of the water according to its density.

Essential oils have a penetrating odour and acrid taste, which are often pleasant when sufficiently diluted. They are soluble in alcohol, though in different proportions. They are not appreciably dissolved by water; but that fluid acquires the odour of the oil with which it is distilled. With the fixed oils they unite in every proportion, and are sometimes adulterated with them, an imposition easily detected by the mixed oil causing on paper a greasy stain, which is not removed by heat.

Volatile oils burn in the open air with a clear white light, and the sole products of the combustion are water and carbonic acid. On exposure to the atmosphere, they gradually absorb a large quantity of oxygen, in consequence of which they become thick, and are at length converted into a substance resembling resin. This change is rendered more rapid by the agency of light.

Of the acids, the action of strong nitric acid on volatile oils is the most energetic, being often attended with vivid combustion,—an effect which is rendered more certain by previously adding to the nitric a few drops of sulphuric acid.

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\* *Recherches sur les Corps gras.*

Volatile oils do not unite readily with metallic oxides, and are attacked with difficulty even by the alkalies. The substance called Starkey's soap is made by triturating oil of turpentine with an alkali.

Volatile oils dissolve sulphur in large quantity, forming a deep brown coloured liquid, called *balsam of sulphur*. The solution is best made by boiling flowers of sulphur in spirit of turpentine. Phosphorus may likewise be dissolved by the same menstruum.

The most interesting of the essential oils are those of turpentine, caraway, cloves, peppermint, nutmeg, anise, lavender, cinnamon, citron, and chamomile. Of these the most important is the first, which is much employed in the preparation of varnishes, and for some medical and chemical purposes. It is procured by distilling common turpentine; and when purified by a second distillation, it is *spirit* or *essence* of turpentine.

Common oil of turpentine is inferred by Dr Ure to consist of carbon 14 atoms, oxygen 1 atom, and hydrogen 10 atoms\*. According to M. Houton Labillardière, the purified oil contains no oxygen, but is composed of carbon and hydrogen in such proportions, that one volume of its vapour contains 4 volumes of olefiant gas, and two volumes of the vapour of carbon†.

*Camphor*.—This inflammable substance, which in several respects is closely allied to the essential oils, exists ready formed in the *Laurus camphora* of Japan, and is obtained from its trunk, root, and branches by sublimation.

Camphor has a bitterish, aromatic, pungent taste, accompanied with a sense of coolness. It is unctuous to the touch, and brittle; but it possesses a degree of toughness which prevents it from being pulverized with facility. It is easily reduced to powder by trituration with a few drops of alcohol. Its specific gravity is 0.988. It is exceedingly volatile, being gradually dissipated in vapour if kept in open vessels. At 288° F. it enters into fusion, and boils at 400° F.

Camphor is insoluble in water; but when triturated with sugar, and then mixed with that fluid, a portion is dissolved sufficient for communicating its flavour. It is dissolved freely by alcohol, and is thrown down by the addition of water. It is likewise soluble in the fixed and volatile oils, and in strong acetic acid. Sulphuric acid decomposes camphor, converting it into a substance like artificial tannin. (Mr Hatchett.) With the nitric it yields camphoric acid.

Camphor, according to the analysis of Dr Ure, appears to consist of carbon ten atoms, oxygen one atom, and hydrogen nine atoms.

On transmitting a current of muriatic acid gas through the purified oil of turpentine, surrounded by a mixture of snow and salt, a quantity of the gas is absorbed equal to one-third of the weight of the oil, and a white crystalline substance, very similar to camphor, is generated. This matter was discovered by Kind, and has since been studied by Trommsdorf, Gehlen, and Thénard. The last chemist maintains that this peculiar substance is a compound of turpentine and muriatic acid, a view which is supported by the researches of M. Houton Labillardière.

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\* Philosophical Transactions for 1822.

† Journal de Pharmacie, vol. iv.

## Resins.

Resins are the inspissated juices of plants, and commonly occur either pure or in combination with an essential oil. They are solid at common temperatures, brittle, inodorous, and insipid. They are non-conductors of electricity, and when rubbed become negatively electric. They are generally of a yellow colour, and semi-transparent.

Resins are fused by the application of heat, and by a still higher temperature are decomposed. In close vessels they yield empyreumatic oil, and a large quantity of carburetted hydrogen, a small residue of charcoal remaining. In the open air they burn with a yellow flame and much smoke, being resolved into carbonic acid and water.

Resins are dissolved by alcohol, ether and the essential oils, and the alcoholic and ethereal solutions are precipitated by water, a fluid in which they are quite insoluble. Their best solvent is pure potassa and soda, and they are also soluble in the alkaline carbonates by the aid of heat. The product is in each case a soapy compound, which is decomposed by an acid.

Concentrated sulphuric acid dissolves resins; but the acid and the resin mutually decompose each other, with disengagement of sulphurous acid, and deposition of charcoal. Nitric acid acts upon them with violence, converting them into a species of tannin, which was discovered by Mr Hatchett. No oxalic acid is formed during the action.

The uses of resin are various. Melted with wax and oil, resins constitute ointments and plasters. Combined with oil or alcohol, they form different kinds of oil and spirit varnish. Sealing-wax is composed of lac, Venice turpentine, and common resin. The composition is coloured black, by means of lamp-black, or red by cinnabar or red lead. Lamp-black is the soot of imperfectly burned resin.

Of the different resins the most important are common resin, copal, lac, sandarach, mastich, elemi, and dragon's blood. The first is procured by heating turpentine, which consists of oil of turpentine and resin, so as to expel the volatile oil. The common turpentine, obtained by incisions made in the trunk of the Scotch fir tree, (*Pinus sylvestris*) is employed for this purpose; but the other kinds of turpentine, such as the Venice turpentine, from the larch, (*Pinus larix*) the Canadian turpentine from the *Pinus balsamea*, or the Strasburgh turpentine, from the *Pinus picea*, yield resin by a similar treatment.

When turpentine is extracted from the wood of the fir tree by heat, partial decomposition ensues, and a dark substance, consisting of resin, empyreumatic oil, and acetic acid, is the product. This constitutes tar; and when inspissated by boiling, it forms pitch.

Considerable uncertainty prevails as to the composition of common resin, as will appear by the following statement:—

	Gay-Lussac and Thénard.	Thomson.	Ure.
Carbon,	75.944	63.15	75.00
Oxygen,	13.337	25.26	12.50
Hydrogen,	10.719	11.59	12.50
	<hr/>	<hr/>	<hr/>
	100	100	100

**Amber.**—This substance is found chiefly on the coasts of Prussia,

**Livonia, Pomerania, and Denmark**, occurring sometimes on the shore, and sometimes in beds of bituminous wood. It is undoubtedly of vegetable origin, and has the general properties of a resin; but it differs from resinous substances in yielding succinic acid, when heated in close vessels.

**Balsams.**—The balsams are native compounds of resin and benzoic acid, and issue from incisions made in the trees, which contain them, in the same manner as turpentine from the fir. Some of them, such as storax and benzoin, are solid; while others, of which the balsams of Tolu and Peru are examples, are viscid fluids.

**Gum Resins.**—The substances to which this name is applied are the concrete juices of certain plants, and consist of resin, essential oil, gum, and extractive vegetable matter. The two former principles are dissolved by alcohol, and the two latter in water. Their proper solvent, therefore, is proof spirit. Under the class of gum resins are comprehended several valuable medicines, such as aloes, ammoniacum, assafoetida, euphorbium, galbanum, gamboge, myrrh, scammony, and guaiacum.

**Caoutchouc**, commonly called elastic gum or Indian rubber, is the concrete juice of the *Hevea caoutchouc* and *Iatropa elastica*, natives of South America, and of the *Ficus Indica* and *Artocarpus integrifolia*, which grow in the East Indies. It is a soft yielding solid, of a whitish colour when not blackened by smoke, possesses considerable tenacity, and is particularly remarkable for its elasticity. It is inflammable, and burns with a bright flame. When cautiously heated, it fuses without decomposition. It is insoluble in water and alcohol; but it dissolves, though with some difficulty, in pure ether. It is very sparingly dissolved by the alkalies, but its elasticity is destroyed by their action. By the sulphuric and nitric acids it is decomposed, the former causing a deposition of charcoal, and the latter a formation of oxalic acid.

Caoutchouc is soluble in the essential oils, in petroleum, and in cajeput oil, and may be procured by evaporation from the two latter without loss of its elasticity. The purified naphtha from coal tar dissolves it readily, and as the solvent is cheap, and the properties of the caoutchouc are unaltered by the process, the solution may be conveniently employed for forming elastic tubes, or other apparatus of a similar kind. It is used by Mr Mackintosh of Glasgow for covering cloth with a thin stratum of caoutchouc, so as to render it impermeable to moisture. This property of coal naphtha was discovered by Mr James Syme, Lecturer on Surgery in this city. (*Annals of Philosophy*, vol. xii.)

The composition of caoutchouc has not been determined in a satisfactory manner. According to the analysis of Dr Ure, 100 parts of it consist of carbon 90, oxygen 0.88, and hydrogen 9.12. But caoutchouc yields ammonia when heated in close vessels, and therefore must contain nitrogen as one of its constituents, a principle which was not detected by Dr Ure.

**Wax.**—This substance, which partakes of the nature of a fixed oil, is an abundant vegetable production, entering into the composition of the pollen of flowers, covering the envelope of the plumb and other fruit, especially the berries of the *Myrica cerifera*, and in many instances forming a kind of varnish to the surface of leaves. From this circumstance it was long supposed that wax is solely of vegetable origin, and that the wax of the honey-comb is derived from flowers only;



but it appears from the observations of Huber that it must likewise be regarded as an animal product, since he found bees to deposit wax though fed on nothing but sugar.

Common wax is always more or less coloured, and has a distinct peculiar odour, of both which it may be deprived by exposure in thin slices to light, air, and moisture, or more speedily by the action of chlorine. At ordinary temperatures it is solid, and somewhat brittle; but it may easily be cut with a knife, and the fresh surface presents a characteristic appearance, to which the name of waxy lustre is applied. Its specific gravity is 0.96. At about 150° F. it enters into fusion, and boils at a high temperature. Heated to redness in close vessels it suffers complete decomposition, yielding products very similar to those which are procured under the same circumstances from oil. As it burns with a clear white light, it is employed for forming candles.

Wax is insoluble in water, and is only sparingly dissolved by boiling alcohol or ether, from which the greater part is deposited on cooling. It is readily attacked by the fixed alkalies, being converted into a soap which is soluble in hot water. It unites by the aid of heat in every proportion with the fixed and volatile oils, and with resin. With different quantities of oil it constitutes the simple liniment, ointment, and cerate of the pharmacopœia.

Wax, according to the observations of John, consists of two different principles, one of which is soluble and the other insoluble in alcohol. To the former he has given the name of *cerin*, and to the latter of *myrcin*. From the ultimate analysis of Dr Ure, whose result corresponds closely with that of Gay-Lussac and Thénard, 100 parts of wax are composed of carbon 80.4, oxygen 8.3, and hydrogen 11.3; from which it is probable that it consists of 13 atoms of the first element, 1 atom of the second, and 11 atoms of the third.

### Alcohol.

Alcohol is the intoxicating ingredient of all spirituous and vinous liquors. It does not exist ready formed in plants, but is a product of the vinous fermentation, the theory of which will be stated in a subsequent section.

Common alcohol or spirit of wine is prepared by distilling whiskey or some ardent spirit, and the rectified spirit of wine is procured by a second distillation. The first has a specific gravity of about 0.867, and the last at 0.835 or 0.84. In this state it contains a quantity of water, of which it may be freed by the action of substances which have a strong affinity for that liquid. Thus, when the carbonate of potassa, heated to about 300° F., is mixed with spirit of wine, the alkali unites with the water, forming a dense solution, which, on standing, separates from the alcohol, so that the latter may be removed by decantation. To the alcohol, thus deprived of a part of its water, fresh portions of the dry carbonate are successively added, until it falls through the spirit without being moistened. Other substances, which have a powerful attraction for water, may be substituted for the carbonate of potassa. Gay-Lussac recommends the use of pure lime or baryta; (An. de Ch. vol. lxxxvi.) and dry alumina may also be employed with advantage. A very convenient process is to mix the alcohol with the chloride of calcium, in powder, or with quicklime, and draw off the stronger portions by distillation. Another process for depriving alcohol of water is to put it into the bladder of an ox, and sus-

pend it over a sand bath. The water gradually passes through the coats of the bladder, while the pure alcohol is retained. (Journal of Science, vol. xviii.) The strongest alcohol which can be procured by any of these processes has a specific gravity of 0.796 at 60° F. This is called *absolute* alcohol, on the supposition of its being quite free from water.

Alcohol is a colourless elastic fluid, of a penetrating odour, and burning taste. It is highly volatile, boiling, when its density is 0.820. at the temperature of 176° F. The specific gravity of its vapour, according to Gay-Lussac, is 1.613. Like volatile liquids in general, it produces a considerable degree of cold during its evaporation. Of all fluids it is the only one which has not hitherto been congealed. Mr Hutton, indeed, announced in the 34th volume of Nicholson's Journal, that he had succeeded in freezing alcohol; but the fact itself is regarded as doubtful, since no description of the method has hitherto been published. In the experiments of Mr Walker, alcohol was found to retain its fluidity at—91° F.

Alcohol is highly inflammable, and burns with a lambent yellowish-blue flame. Its colour varies considerably with the strength of the alcohol, the blue tint predominating when it is strong, and the yellow when it is diluted. The combustion is not attended with the least degree of smoke, and the sole products are water and carbonic acid. When transmitted through a red-hot tube of porcelain, it is resolved into carburetted hydrogen, carbonic oxide, and water, and the tube is lined with a small quantity of charcoal.

Alcohol unites with water in every proportion. The act of combining is usually attended with diminution of volume, so that a mixture of 50 measures of alcohol and 50 of water occupies less than 100 measures. Owing to this circumstance the action is accompanied with an increase of temperature. Since the density of the mixture increases as the water predominates, the strength of the spirit may be estimated by its specific gravity. Equal weights of absolute alcohol and water constitute *proof spirit*, the density of which is 0.917; but the proof spirit employed by the colleges for tinctures has a specific gravity of 0.930, or 0.935.

Of the salifiable bases alcohol can alone dissolve potassa, soda, lithia, ammonia, and the vegetable alkalies. None of the earths, or other metallic oxides, are dissolved by it. Most of the acids attack it by the aid of heat, giving rise to a class of bodies to which the name of *ether* is applied. All the salts which are either insoluble, or sparingly soluble in water, are insoluble in alcohol. The efflorescent salts are, likewise, for the most part insoluble in this menstruum; but, on the contrary, it is capable of dissolving all the deliquescent salts, except the carbonate of potassa. Many of the vegetable principles, such as sugar, manna, camphor, resins, balsams, and the essential oils, are soluble in alcohol.

The constitution of alcohol has been ably investigated by M. Sausure, jun. (An. de Ch. vol. lxxxix.) According to his analysis, which was made by transmitting the vapour of absolute alcohol through a red-hot porcelain tube, and examining the products, this fluid is composed of carbon 51.98, oxygen 34.32, and hydrogen 13.70. From these data, alcohol is inferred to consist of

Carbon,	.	12	2 atoms	.	52.17
Oxygen,	.	8	1 atom	.	34.79
Hydrogen,	.	3	3 atoms	.	13.04

These numbers, it is obvious, are in such proportion that alcohol may be regarded as a compound of 14 parts or one atom of olefiant gas, and 9 parts or one atom of water.

Knowing the composition of alcohol by weight, it is easy to calculate the proportion of its constituents by measure. For this purpose it is only necessary to divide 14 by 0.972, (the sp. gr. of olefiant gas) and 9 by 0.625, (the sp. gr. of aqueous vapour); and as the quotients are very nearly equal, it follows that alcohol must consist of equal measures of aqueous vapour and olefiant gas. It is inferred, also, that these two gaseous bodies, in uniting to form the vapour of alcohol, occupy half the space which they possessed separately; because the density of the vapour of alcohol, as calculated on this supposition, ( $0.9722 + 0.625 = 1.5972$ ) corresponds closely with 1.613, the number which was ascertained experimentally by Gay-Lussac.

Considerable uncertainty prevailed a few years ago as to the state in which alcohol exists in wine. Some were of opinion that it is generated by the heat employed in the distillation, while others thought that the alcohol is merely separated during the process. This question was finally determined by Mr Brande, who made it the subject of two essays which were published in the Philosophical Transactions for 1811 and 1813. He there demonstrated that the alcohol exists ready formed in wine, by separating that principle without the aid of heat. His method consists in precipitating the acid and extractive colouring matters of the wine by the sub-acetate of lead, and then depriving the alcohol of water by dry carbonate of potassa, in the way already mentioned. The pure alcohol, which rises to the surface, is then measured by means of a narrow graduated glass tube. The same fact has since been established by the experiments of Gay-Lussac, who procured alcohol from wine by distilling it *in vacuo* at the temperature of 60° F. He also succeeded in separating the alcohol by the method of Mr Brande; but he suggests the employment of litharge in fine powder, instead of the sub-acetate of lead, for precipitating the colouring matter. (Mém. d'Arcueil, vol. iii.)

The preceding researches of Mr Brande led him to examine the quantity of alcohol contained in spirituous and fermented liquors. According to his experiments, brandy, rum, gin, and whiskey, contain from 51 to 54 per cent. of alcohol, of specific gravity 0.825. The stronger wines, such as Lissa, Raisin wine, Marsala, Port, Madeira, Sherry, Teneriffe, Constantia, Malaga, Bucellas, Calcavella, and Vidonia, contain from between 18 or 19 to 25 per cent. of alcohol. In Claret, Sauterne, Burgundy, Hock, Champagne, Hermitage, and Gooseberry wine, the quantity is from 12 to 17 per cent. In cyder, perry, ale, and porter, the quantity varies from 4 to near 10 per cent. In all spirits, such as brandy or whiskey, the alcohol is simply combined with water; whereas in wine it is in combination with mucilaginous, saccharine, and other vegetable principles, a condition which tends to diminish the action of the alcohol upon the system. This may, perhaps, account for the fact that brandy, which contains little more than twice as much real alcohol as good port wine, has an intoxicating power which is considerably more than double.

### Ether.

The name *ether* was formerly employed to designate the volatile inflammable liquid which is formed by heating a mixture of alcohol and sulphuric acid; but the same term has since been extended to several

other compounds produced by the action of acids on alcohol, and which, from their volatility and inflammability, were supposed to be identical or nearly so with sulphuric ether. It appears however from the researches of several chemists, but especially of M. Thénard, that ethers, though analogous in their leading properties, frequently differ both in composition and in their mode of formation. (*Mémoires d'Arceuil*, vol. i. and ii.)

*Sulphuric ether*.—In forming this compound, strong sulphuric acid is gently poured upon an equal weight of rectified spirit of wine contained in a thin glass retort, and after mixing the fluids together by agitation, which occasions a free disengagement of caloric, the mixture is heated as rapidly as possible until ebullition commences. At the beginning of the process nothing but alcohol passes over; but as soon as the liquid boils, ether is generated, and condenses in the recipient, which is purposely kept cool by the application of ice or moist cloths. When a quantity of ether is collected, equal in general to about half of the alcohol employed, white fumes begin to appear in the retort. At this period, the process should be discontinued, or the receiver be changed; for although ether does not cease to be generated, its quantity is less considerable, and several other products make their appearance. Thus on continuing the operation, sulphurous acid is disengaged, and a yellowish liquid, commonly called *ethereal oil* or *oil of wine*, passes over into the receiver. If the heat be still continued, a large quantity of olefiant gas is disengaged, and all the phenomena ensue which were mentioned in the description of that compound. (Page 194.)

Ether, thus formed, is always mixed with alcohol, and generally with some sulphurous acid. To separate these impurities the ether should be agitated with a strong solution of potassa, which neutralizes the acid, while the water unites with the alcohol. The ether is then distilled by a very gentle heat, and may be rendered still stronger by distillation from the chloride of calcium.

To comprehend the theory of the formation of ether, it is necessary to compare the composition of this substance with that of alcohol. Ether was analyzed by M. Saussure in the same manner as alcohol; and from the data furnished by his analysis, corrected by Gay-Lussac, (*An. de Ch.* xcv.) ether is inferred to consist of 28 parts or two atoms of olefiant gas, and 9 parts or one atom of water. But alcohol is composed of one atom of olefiant gas and one atom of water; so that, if from two atoms of alcohol we withdraw one atom of water, the remaining elements are in exact proportion for constituting ether. This is the precise mode in which sulphuric acid is supposed to operate in generating ether, an effect which it is well calculated to produce, owing to its strong affinity for moisture. (Page 154.) This view was first proposed by Fourcroy and Vauquelin, and accounts for the phenomena in a very satisfactory manner. These chemists, it is true, erred in thinking that the sulphuric acid occasions no other change; since subsequent observation has proved that the sulpho-vinic acid, to the constitution of which sulphuric acid is essential, is formed even at the very commencement of the process. Notwithstanding this error, however, the production of ether may be justly ascribed to the sulphuric acid abstracting water or its elements from the alcohol, an opinion which is supported by various circumstances. Thus it accounts for the disengagement of sulphurous acid and olefiant gas towards the middle and close of the process; for since the elements of



the alcohol alone contribute to the formation of ether, while all the sulphuric acid remains in the retort, and most of it in a free state, it is apparent that the relative quantities of alcohol and acid must be continually changing during the operation, until at length the latter predominates so greatly as to be able to deprive the former of all its water, and thus give rise to the disengagement of olefiant gas. (Page 194.) Accordingly it is well known, that if fresh alcohol be added as soon as the production of pure ether ceases, an additional quantity of that substance will be produced. It follows, also, from the same doctrine, that the power of the same portion of acid in forming ether must be limited, because it gradually becomes so diluted with water, that it is at last unable to disunite the elements of the alcohol. Consistently with the same view, it is found that ether, precisely analogous to that from sulphuric acid, may be prepared by digesting alcohol with other acids which have a strong affinity for water, as for example with phosphoric, arsenic, and fluoboric acids.

The production of a peculiar acid in the preceding process was first noticed by M. Dabit, about the year 1800. The substance, to which the name of *sulpho-vinic* acid is applied, has since been examined by Sertuerner, Vogel, and Gay-Lussac, and the two last mentioned philosophers regarded it as a compound of hyposulphuric acid and a peculiar vegetable matter. Mr Hennel, however, has lately given a different, and to all appearance a more correct view of its nature. According to this chemist, sulpho-vinic acid and the oil of wine are both composed of sulphuric acid and carburet of hydrogen. The oil of wine, which has no acid reaction when pure, consists of 2 atoms of sulphuric acid, 8 of carbon, and 8 of hydrogen. When heated, it parts with half of its carbon and hydrogen, and sulpho-vinic acid remains, consisting of 2 atoms of sulphuric acid, 4 of carbon, and 4 of hydrogen. (Journal of Science, xxi. p. 331.)

Sulphuric ether is a colourless fluid, of a hot pungent taste, and fragrant odour. Its specific gravity in its purest form is about 0.700, or according to Lovitz 0.632; but that of the shops is 0.74 or even lower, owing to the presence of alcohol. Its volatility is exceedingly great:—Under the atmospheric pressure, ether of density 0.720 boils at 96° or 98° F., and at about—40° F. in a vacuum. (Black's Lectures, vol. i. p. 151.) Its evaporation, from the rapidity with which it takes place, occasions intense cold, sufficient under favourable circumstances for freezing mercury. Its vapour has a density of 2.586. At 46 degrees below zero of Fahr. it congeals.

Ether combines with alcohol in every proportion, but it is very sparingly soluble in water. When agitated with that fluid, the greater part separates on standing, a small quantity being retained, which imparts an ethereal odour to the water. The ether so washed is very pure, because the water retains the alcohol which had been mixed with it.

Ether is highly inflammable, burning with a blue flame, and formation of water and carbonic acid. With oxygen gas its vapour forms a mixture, which explodes violently on the approach of flame, or by the electric spark. On being transmitted through a red-hot porcelain tube it undergoes decomposition, and yields the same products as alcohol.

When a coil of platinum wire is heated to redness, and then suspended above the surface of ether contained in an open vessel, the wire instantly begins to glow, and continues in that state until all the ether is consumed. (Davy.) During this slow combustion, pungent



acid fumes are emitted, which, if received in a separate vessel, condense into a colourless liquid possessed of acid properties. Mr Daniell, who prepared a large quantity of it, was at first inclined to regard it as a new acid, and described it under the name of *lampic acid*; but he has since ascertained that its acidity is owing to the acetic acid, which is combined with some compound of carbon and hydrogen different both from ether and alcohol. (Journal of Science, vol. vi. and xii.)

If ether is exposed to light in a vessel partially filled, and which is frequently opened, it gradually absorbs oxygen, and a portion of acetic acid is generated. This change was first noticed by M. Planche, and has been confirmed by Gay-Lussac. (An. de Ch. et de Ph. vol. ii.)

The solvent properties of ether are less extensive than those of alcohol. It dissolves the essential oils and resins, and some of the vegetable alkalies are soluble in it. It unites also with ammonia; but the fixed alkalies are insoluble in this menstruum.

*Nitrous ether.*—This compound is prepared by distilling a mixture of concentrated nitric acid with an equal weight of alcohol; but as the reaction is apt to be exceedingly violent, the process should be conducted with extreme care. The safest method is to add the acid to the alcohol by small quantities at a time, allowing the mixture to cool after each addition before more acid is added. The distillation is then conducted at a very gentle temperature, and the ether collected in a Woulfe's apparatus. The theory of the process is in some respects obscure; but as the formation of ether is attended with the disengagement of the protoxide and deutoxide of nitrogen, together with free nitrogen and carbonic acid, it follows that the alcohol and acid mutually decompose each other. It appears, however, from the experiments of Thénard, that this ether is a compound of alcohol and nitrous acid; and, consequently, the essential change must consist in the conversion of nitric into nitrous acid at the expense of one part of the alcohol, while the remainder of that fluid combines with the nitrous acid. Consistently with this view, nitrous ether may be made directly by the action of anhydrous nitrous acid on pure alcohol.

The nitrous agrees with sulphuric ether in its leading properties; but it is still more volatile. When recently distilled from quicklime by a gentle heat, it is quite neutral; but it soon becomes acid by keeping. The products of its spontaneous decomposition are alcohol, nitrous acid, and a little acetic acid. A similar change is instantly effected by mixing the ether with water, or distilling it at a high temperature. It is also decomposed by potassa, and, on evaporation, crystals of the nitrite or hyponitrite of that alkali are deposited. (Mémoires d'Arcueil, vol. i.)

*Acetic ether.*—This ether is analogous in composition to the preceding, and is formed by distilling acetic acid with an equal weight of alcohol. When set on fire, it burns with disengagement of acetic acid; and when mixed with a strong solution of potassa, and subjected to distillation, pure alcohol passes over, and the acetate of potassa remains in the retort. It is hence inferred to consist of acetic acid and alcohol. When pure it is quite neutral.

According to Thénard, the acetic is the only vegetable acid which forms ether by being heated alone with alcohol. Ether may also be generated by treating the tartaric, oxalic, malic, citric, or benzoic acid with a mixture of alcohol and sulphuric acid, and Thénard regards these ethers as compounds of a vegetable acid with alcohol; but the employment of a mineral acid in producing them renders additional

experiments necessary before a decisive opinion can be formed concerning their composition.

*Muriatic ether.*—This compound, which is prepared by distilling a mixture of concentrated muriatic acid and pure alcohol, was supposed by Thénard to be analogous in composition to nitrous ether. It appears, however, from the experiments of MM. Robiquet and Colin, that it consists of muriatic acid and the elements of olefiant gas, and is therefore quite free from oxygen. (An. de Ch. et de Ph. vol. ii.) It does not affect the colour of litmus paper, volatilizes still more rapidly than sulphuric ether, and is highly inflammable. Its combustion is attended with the disengagement of a large quantity of muriatic acid gas.

*Hydriodic ether*, first prepared by Gay-Lussac, appears to be similar in composition to muriatic ether.

### Bituminous Substances.

Under this title are included several inflammable substances which, though of vegetable origin, are found in the earth, or issue from its surface. They may be conveniently arranged under the two heads of bitumen and pit-coal. The first comprehends naphtha, petroleum, mineral tar, mineral pitch, asphaltum, and retinasphaltum, of which the three first mentioned are liquid, and the others solid. The second comprises brown coal, the different varieties of *common* or *black coal*, and *glance coal*.

*Bitumen.*—*Naphtha* is a volatile limpid liquid, of a strong peculiar odour, and light yellow colour. Its specific gravity, when highly rectified, is 0.758. It is very inflammable, and burns with a white flame mixed with much smoke. At 186° F. it enters into ebullition, and its vapour has a density of 2.833. (Saussure.) It retains its liquid form at zero of Fahrenheit. It is insoluble in water, and very soluble in alcohol; but it unites in every proportion with sulphuric ether, petroleum, and oils. It appears from the observations of Saussure to undergo no change by keeping, even in contact with air.

Naphtha contains no oxygen, and is hence employed for protecting the more oxidable metals, such as potassium and sodium, from oxidation. According to the analysis of Saussure, it is composed of carbon and hydrogen in the proportion of six atoms of the former to five of the latter. Dr Thomson states the composition of naphtha from coal tar, which seems identical with mineral naphtha, to consist of six atoms of carbon and six of hydrogen. (Page 198.)

Naphtha occurs in some parts of Italy, and on the banks of the Caspian Sea. It may be procured also by distillation from petroleum.

*Petroleum* is much less limpid than naphtha, has a reddish-brown colour, and is unctuous to the touch. It is found in several parts of Britain and the continent of Europe, in the West-Indies, and in Persia. It occurs particularly in coal districts. The *mineral tar* is very similar to petroleum, but is more viscid and of a deeper colour. Both these species become thick by exposure to the atmosphere, and in the opinion of Mr Hatchett pass into solid bitumen.

*Asphaltum* is a solid brittle bitumen of a black colour, vitreous lustre, and conchoidal fracture. It melts easily, and is very inflammable. It emits a bituminous odour when rubbed, and by distillation yields a fluid like naphtha. It is soluble in about five times its weight of

naphtha, and the solution forms a good varnish. It is rather denser than water.

Asphaltum is found on the surface and on the banks of the Dead Sea, and occurs in large quantity in Barbadoes and Trinidad. It was employed by the ancients in building, and is said to have been used by the Egyptians in embalming.

*Mineral Pitch* or *Maltha* is likewise a solid bitumen, but is much softer than asphaltum. The elastic bitumen, or *mineral caoutchouc*, is a rare variety of mineral pitch, found only in the Odin mine, near Castleton in Derbyshire.

*Retinasphaltum* is a peculiar bituminous substance, found associated with the brown coal of Bovey in Devonshire, and described by Mr Hatchett in the Philosophical Transactions for 1804. It consists partly of bitumen, and partly of resin, a composition which led Mr Hatchett to the opinion that bitumens are chiefly formed from the resinous principle of plants.

*Pit Coal*.—The *brown coal* is characterized by burning with a peculiar bituminous odour, like that of peat. It is sometimes earthy, but the fibrous structure of the wood from which it is derived is generally more or less distinct, and hence this variety is called *bituminous wood*. The *pitch coal* or *jet*, which is employed for forming ear-rings and other trinkets, is intermediate between brown and black coal, but is perhaps more closely allied to the former than the latter.

Brown coal is found at Bovey in Devonshire, (Bovey coal) in Iceland, where it is called *surturbrand*, and in several parts of the continent, especially at the Meissner in Hessa, in Saxony, Prussia, and Styria.

Of the *black* or *common coal* there are several varieties, which differ from each other, not only in the quantity of foreign matters, such as the sulphuret of iron and earthy substances which they contain, but also in the proportion of what may be regarded as essential constituents. Thus some kinds of coal consist almost entirely of carbonaceous matters, and therefore form little flame in burning; while others, of which the cannel coal is an example, yield a large quantity of inflammable gases by heat, and consequently burn with a large flame.

Dr Thomson has arranged the different kinds of coal which are met with in Britain into four subdivisions. (An. of Phil. vol. xiv.) The first is *caking coal*, because its particles are softened by heat and adhere together, forming a compact mass. The coal found at Newcastle, around Manchester, and in many other parts of England, is of this kind. The second is termed *splint coal*, from the splintery appearance of its fracture. The *cherry coal* occurs in Staffordshire, and in the neighbourhood of Glasgow. Its structure is slaty, and it is more easily broken than the splint coal, which is much harder. It easily takes fire, and is consumed rapidly, burning with a clear yellow flame. The fourth kind is the *cannel coal*, which is found of peculiar purity at Wigan in Lancashire. In Scotland it is known by the name of *parrot coal*. From the brilliancy of the light which it emits while burning, it is sometimes used as a substitute for candles, a practice which is said to have led to the name of *cannel coal*. It has a very compact structure, does not soil the fingers when handled, and admits of being polished. Snuff-boxes and other ornaments are made with this coal; and it is peculiarly well fitted for forming coal gas. According

to the experiments of Dr Thomson, these varieties of coal are thus constituted :

	<i>Caking Coal.</i>	<i>Splint Coal.</i>	<i>Cherry Coal.</i>	<i>Cannel Coal.</i>
Carbon,	75.28	75.00	74.45	64.72
Hydrogen,	4.18	6.25	12.40	21.56
Nitrogen,	15.96	6.25	10.22	13.72
Oxygen,	4.58	12.50	2.93	0.00
	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00

Judging from the quantity of oxidized products (water, carbonic acid, and carbonic oxide,) which are procured during the distillation of coal, Dr Henry infers that coal contains more oxygen than was found by Thomson. (Elements, 10th Edition, vol. ii. p. 321.) This opinion is supported by the analysis of Dr Ure, who found 26.6 per cent. of oxygen in splint, and 21.9 in cannel coal. When coal is heated to redness in close vessels, a great quantity of volatile matter is dissipated, and a carbonaceous residue, called *coke*, remains in the retort. The volatile substances are coal tar, acetic acid, water, sulphuretted hydrogen, and hydrosulphuret and carbonate of ammonia, together with the several gases formerly enumerated. (Page 199.) The greater part of these substances are real products, that is, are generated during the distillation. The bituminous matters probably exist ready formed in coal; but Dr Thomson is of opinion that these are also products, and that coals are atomic compounds of carbon, hydrogen, nitrogen, and oxygen.

*Glance coal.*—Glance coal, or *anthracite*, differs from common coal, which it frequently accompanies, in containing no bituminous substances, and in not yielding inflammable gases by distillation. Its sole combustible ingredient is carbon, and consequently it burns without flame. It commonly occurs in the immediate vicinity of basalt, under circumstances which lead to the suspicion that it is coal from which the volatile ingredients have been expelled by subterranean heat. At the Meissner, in Hessa, it is found between a bed of brown coal and basalt. The Kilkenny coal appears to be a variety of Glance Coal. (Thomson, An. of Phy. vol. xv.)

## SECTION IV.

### SUBSTANCES, THE OXYGEN AND HYDROGEN OF WHICH ARE IN EXACT PROPORTION FOR FORMING WATER.

#### *Sugar.*

Sugar is an abundant vegetable product, existing in a great many ripe fruits, though few of them contain it in sufficient quantity for being collected. The juice which flows from incisions made in the trunk of the American maple tree, is so powerfully saccharine that it may be applied to useful purposes. Sugar was prepared in France and Germany during the late war from the beet root; and Proust ex-

tracted it in Spain from grapes. But all the sugar at present used in Europe is obtained from the sugar-cane, (*Arundo saccharifera*) which contains it in greater quantity than any other plant. The process, as practised in our West India Islands, consists in evaporating the juice of the ripe cane by a moderate and cautious ebullition, until it has attained a proper degree of consistency for crystallizing. During this operation lime water is added, partly for the purpose of neutralizing free acid, and partly to facilitate the separation of extractive and other vegetable matters, which unite with the lime and rise as a scum to the surface. When the syrup is sufficiently concentrated, it is drawn off into shallow wooden coolers, where it becomes a soft solid composed of loose crystalline grains. It is then put into barrels with holes in the bottom, through which a black ropy juice, called molasses or treacle, gradually drops, leaving the crystallized sugar comparatively white and dry. In this state it constitutes the raw or muscovado sugar.

The raw sugar is farther purified by boiling a solution of it with white of eggs, or the serum of bullock's blood, lime water being generally employed at the same time. When properly concentrated, the clarified juice is received in conical earthen vessels, the apex of which is undermost, in order that the fluid parts may collect there, and be afterwards drawn off by the removal of a plug. In this state it is loaf or refined sugar. In the process of refining sugar, it is important to concentrate the syrup by a low temperature; and on this account a very great improvement was introduced some years ago by conducting the evaporation in *vacuo*.

Pure sugar is solid, white, inodorous, and of a very agreeable taste. It is hard and brittle, and when two pieces are rubbed against each other in the dark, phosphorescence is observed. It crystallizes in the form of four or six-sided prisms bevelled at the extremities. The crystals are best made by fixing threads in syrup, which is allowed to evaporate spontaneously in a warm room, and the crystallization is promoted by adding spirit of wine. In this state it is known by the name of *sugarcandy*.

Sugar undergoes no change on exposure to the air; for the deliquescent property of raw sugar is owing to impurities. It is soluble in an equal weight of cold, and to almost any extent in hot water. It is soluble in about four times its weight of boiling alcohol, and the saturated solution, by cooling and spontaneous evaporation, deposits large crystals. When the aqueous solution of sugar is mixed with yeast, it undergoes the vinous fermentation, the theory of which will be explained in a subsequent section.

Sugar unites with the alkalis and alkaline earths, forming compounds in which the taste of the sugar is greatly injured; but it may be obtained again unchanged by neutralizing with sulphuric acid, and dissolving the sugar in alcohol. When boiled with the oxide of lead, it forms an insoluble compound, which consists of 58.26 parts of the oxide of lead, and 41.74 parts of sugar; (Berzelius) but it is not precipitated by the acetate or subacetate of lead.

Sulphuric acid decomposes sugar with deposition of charcoal; and nitric acid causes the production of oxalic acid, as already described in a former section. The vegetable acids diminish the tendency of sugar to crystallize.

Sugar is very easily affected by heat, acquiring a dark colour and burned flavour. At a high temperature it yields the usual products



of the destructive distillation of vegetable matter, together with a considerable quantity of pyromucic acid.

Sugar has been analyzed by Gay-Lussac and Thénard, Berzelius, Ure, Crum, and Prout. According to the analysis of Prout, whose result differs slightly from those of the other chemists, but which is considered by Gay-Lussac as very near the truth, 100 parts of sugar contain 40 parts of carbon, 53.34 of oxygen, and 6.66 of hydrogen, the two last being in exact proportion for forming water. It is difficult to determine the atomic constitution of sugar, but from the preceding data it follows, that its elements are in the ratio of 6 parts or one atom of carbon, to 9 parts or one atom of water; or, by volume, of one measure of the vapour of carbon to one measure of aqueous vapour.

*Molasses*.—The saccharine principle of treacle has been supposed to be different from crystallizable sugar; but it more probably consists of common sugar, which is prevented from crystallizing by the presence of foreign substances such as saline, acid, and other vegetable matters.

*Sugar of grapes*.—The sugar procured from the grape has the essential properties of common sugar. Its taste, however, is not so sweet as common sugar, and according to Saussure it differs slightly in composition, containing a smaller quantity of carbon. The saccharine principle of the acidulous fruits has not been particularly examined. It is obtained with difficulty in a pure state, owing to the presence of vegetable acids, which prevent it from crystallizing. The sugar obtained from the beet root appears identical with common sugar.

A saccharine substance similar to that from grapes may be procured from several vegetable principles, such as starch and the ligneous fibre, by the action of sulphuric acid.

*Honey*.—According to Prout, honey consists of two kinds of saccharine matter, one of which crystallizes readily and is analogous to common sugar, while the other is uncrystallizable. They may be separated by mixing honey with alcohol, and pressing the solution through a piece of linen. The liquid sugar is removed, and the crystallizable portion is left in a solid state. Besides sugar it contains mucilaginous, colouring, and odoriferous matter, and probably a vegetable acid.

The natural history of honey is as yet imperfect. It is uncertain whether honey is merely collected by the bee from the nectaries of flowers, and then deposited in the hive unchanged, or whether the saccharine matter of the flower does not undergo some change in the body of the animal.

*Manna*.—This saccharine matter is the concrete juice of several species of ash, and is procured in particular from the *Fraxinus ornus*. The sweetness of manna is owing, not to sugar, but to a distinct principle called *mannite*, which is mixed with a peculiar vegetable extractive matter. Manna is soluble both in water and boiling alcohol, and the latter, on cooling, deposits pure mannite in the form of minute acicular crystals, which are often arranged in concentrical groups. Mannite differs from sugar, in not fermenting when mixed with water and yeast.

### *Starch or Fecula.—Amidine.*

Starch exists abundantly in the vegetable kingdom, being one of the chief ingredients of most varieties of grain, of some roots, such as

the potato, and of the kernels of leguminous plants. It is easily procured by letting a small current of water fall upon the dough of wheat flour inclosed in a piece of linen, and subjecting it at the same time to pressure between the fingers, until the liquid passes off quite clear. The gluten of the flour is left in a pure state, the saccharine and mucilaginous matters are dissolved, and the starch is washed away mechanically, being deposited from the water on standing in the form of a white powder. An analogous process is practised on a large scale in the preparation of the starch of commerce; and very pure starch may also be obtained in a similar manner from the potato.

Starch is insipid and inodorous, of a white colour, and insoluble in alcohol, ether, and cold water. It does not crystallize; but is commonly found in the shops in six-sided columns of considerable regularity, a form occasioned by the contraction which it suffers in drying. Boiling water acts upon it readily, converting it into a tenacious bulky jelly, which is employed for stiffening linen. In a large quantity of hot water, it is dissolved completely, and is not deposited on cooling. The aqueous solution is precipitated by sub-acetate of lead; but the best test of starch, by which it is distinguished from all other substances, is iodine. This principle forms a blue compound with starch, whether in a solid state or when dissolved in cold water.

Starch unites with the alkalies, forming a compound which is soluble in water, and from which the starch is thrown down by acids. Strong sulphuric acid decomposes it. Nitric acid in the cold dissolves starch; but converts it by the aid of heat into the oxalic and malic acids.

The effects of heat on starch are peculiar, and have lately been examined by M. Caventou. (*An. de Chem. et de Ph.* vol. xxxi.) On exposing dry starch to a temperature a little above 212° F. it acquires a slightly red tint, emits an odour of baked bread, and is rendered soluble in cold water. Starch suffers a similar modification by the action of hot water. Gelatinous starch is generally supposed to be a hydrate of starch; but M. Caventou maintains that the jelly cannot by any method be restored to its original state. He regards this modified starch as identical with the substance described by Saussure under the name of *amidine*. Saussure thought it was generated by exposing a paste made with starch and water for a long time to the air; but according to Caventou, the amidine was formed by the action of the hot water on starch in making the paste. Its essential character is to yield a blue colour with iodine, and to be soluble in cold water. When the solution is gently evaporated to dryness, it yields a transparent mass like horn, which retains its solubility in cold water. When starch is exposed to a still higher temperature than is sufficient for converting it into amidine, a more complete change is effected. It now dissolves with much greater facility in cold water, and gives a purple colour to iodine. A similar effect is produced by long continued boiling.

The starch from wheat, according to the analysis of Gay-Lussac and Thénard, is composed, in 100 parts, of carbon 43.55, oxygen 49.68, and hydrogen 6.77; and this result agrees with the analysis of potato starch made by Berzelius. The proportion of the constituents of starch is therefore very analogous to that of sugar, a circumstance which will account for the conversion of the former into the latter. This change is effected in seeds at the period of germination, and is particularly exemplified in the process of melting barley, during which

the starch of that grain is converted into sugar. Proust\* finds that barley contains a peculiar principle which he calls *hordein*, and which he conceived to be converted in malting partly into starch and partly into sugar. Dr Thomson is of opinion that hordein should rather be regarded as a modification of starch than as a distinct proximate principle†. A similar conversion of starch into sugar appears in some instances to be the effect of frost, as in the potato, apple, and parsnip.

If starch is boiled for a considerable time in water acidulated with 1-12th of its weight of sulphuric acid, it is wholly converted into a saccharine matter similar to that of the grape. This fact was first observed by Kirchoff, and has since been particularly examined by Vogel, De la Rive, and Saussure. It has been established by Saussure that the oxygen of the air exerts no influence over the process, that no gas is disengaged, that the quantity of acid suffers no diminution, and that 100 parts of starch yield 110.14 of sugar. By careful analysis, he found that the only difference in the composition of the starch and sugar is, that the latter contains more of the elements of water than the former. He hence inferred that the starch is converted into sugar by its elements combining with a certain quantity of oxygen and hydrogen in the proportion to form water; and that the acid acts only by increasing the fluidity of the mass. (An. of Philosophy, vol. vi.) Saussure also found that a large quantity of saccharine matter is produced, when gelatinous starch or amidine is kept for a long time either with or without the excess of air. (An. de Ch. et de Ph. vol. xi.)

The recent researches of M. Caventou, already referred to, have thrown considerable light on the chemical nature of several of the amylaceous principles of commerce. The *Indian arrow root*, which is prepared from the root of the *Maranta arundinacea*, has all the characters of pure starch. Sago, obtained from the pith of an East Indian palm tree, (*Cycas circinalis*) and tapioca, from the root of the *Iatropa Manihot*, are chemically the same substance. They both exist in the plants from which they are extracted in the form of starch; but as heat is employed in their preparation, the starch is more or less completely converted into amidine. It hence follows that pure potato starch may be used instead of arrow root, and that the same material, modified by heat, would afford a good substitute for sago and tapioca. Salep, which is obtained from the *Orchis mascula*, consists almost entirely of the substance called *bassorin*, together with a small quantity of gum and starch.

### Gum.

Gum is a common proximate principle of vegetables, and is not confined to any particular part of plants. The purest variety is the gum arabic, the concrete juice of several species of the *Mimosa* or *Acacia*, natives of Africa and Arabia.

Gum arabic occurs in small rounded, transparent, friable grains, commonly of a pale yellow colour, inodorous, and nearly tasteless. It softens when put into water, and then dissolves, forming a viscid solution called *mucilage*. It is insoluble in alcohol and ether, and the former precipitates gum from its solution in water in the form of opaque white flakes. It is soluble both in alkaline solutions and in

\* An. de Ch. et de Ph. vol. v.

† Annals of Philosophy, vol. x.

lime water, and is precipitated unchanged by acids. The dilute acids dissolve, and the concentrated acids decompose gum. Sulphuric acid causes the formation of water and acetic acid, and deposition of charcoal. Digested with strong nitric acid, it yields saccholactic acid, a property which forms a good character for gum. The malic and oxalic acids are generated at the same time.

The aqueous solution of gum may be preserved a considerable time without alteration; but at length it becomes sour, and exhales an odour of acetic acid; a change which takes place without exposure to the air, and must therefore be owing to a new arrangement of its own elements.

Gum is precipitated from its solution in water by several metallic salts, and especially by the sub-acetate of lead, which occasions a curdy precipitate, consisting of 38.25 parts of the oxide of lead and 61.75 parts of gum. (Berzelius.)

When gum is heated to redness in close vessels, it yields, in addition to the usual products, a small quantity of ammonia, which is probably derived from some impurity. It affords a large residue of ash, when burned, which amounts to three per cent., and consists chiefly of the carbonate, together with some phosphate of lime, and a little iron.

From the analysis of Gay-Lussac and Thénard, it appears that 100 parts of gum arabic consist of carbon 42.23, oxygen 50.84, and hydrogen 6.93. This result corresponds very closely with that of Berzelius.

Besides gum arabic there are several well-marked kinds of this principle, especially the gum tragacanth, cherry tree gum, and the mucilage from linseed. All these varieties, though distinguishable from one another by some peculiarity, have the common character of yielding the saccholactic by the action of nitric acid. (Dr Bostock in Nicholson's Journal, vol. xviii.) The substance called *vegetable jelly*, such as is derived from the currant, appears to be mucilage or some modification of gum combined with vegetable acid.

### Lignin.

*Lignin* or the *woody fibre* constitutes the fibrous structure of vegetable substances, and is the most abundant principle in plants. The different kinds of wood contain about 96 per cent. of lignin. It is prepared by digesting the sawings of any kind of wood successively in alcohol, water, and dilute muriatic acid, until all the substances soluble in these menstrua are removed.

Lignin has neither taste nor odour, undergoes no change by keeping, and is insoluble in alcohol, water, and the dilute acids. By digestion in a concentrated solution of pure potassa, it is converted, according to M. Braconnot, into a substance similar to ulmin. Mixed with strong sulphuric acid it suffers decomposition, and is changed into a matter resembling gum; and on boiling the liquid for some time, the mucilage disappears, and a saccharine principle like the sugar of grapes is generated. M. Braconnot finds that several other substances which consist chiefly of woody fibre, such as straw, bark, or linen, yield sugar by a similar treatment. (An. de Ch. et de Ph. vol. xii.) Digested in nitric acid, lignin is converted into the oxalic, malic, and acetic acids.

When the woody fibre is heated in close vessels, it yields a large

quantity of impure acetic acid, (pyroligneous acid) and charcoal of great purity remains in the retort. During this process a peculiar spirituous liquid is formed, which was discovered in 1812 by Mr P. Taylor\*, and has been examined by MM. Macaire and Marcet†, who proposed for it the name of *pyroxylic spirit*. This liquid is similar to alcohol in several of its properties, but differs from it essentially in not yielding ether by the action of sulphuric acid. It has a strong, pungent, ethereal odour, with a flavour like the oil of peppermint. It boils at 150° F. and its density is 0.828. It burns with a blue flame, and without residue. The pyro-acetic spirit, obtained by Mr Chenevix by distilling the acetates of manganese, zinc, and lead, differs from the pyroxylic spirit, not only in composition, but in burning with a yellow flame, and in being miscible in all proportions with the oil of turpentine. The pyroxylic spirit, according to the analysis of Macaire and Marcet, consists of carbon, oxygen, and hydrogen, very nearly in the proportion of 6 atoms of the first, 4 atoms of the second, and 7 atoms of the third; and the pyro-acetic spirit, of carbon 4 atoms, oxygen 2 atoms, and hydrogen 3 atoms. The pyro-acetic spirit appears very similar, if not identical with the pyro-acetic ether of Derosne; and, like the pyroxylic spirit, differs essentially from alcohol in not yielding ether by the action of sulphuric acid. (Page 351.)

The ligneous fibre was found by Gay-Lussac and Thénard to consist of carbon 51.43, oxygen 42.73, and hydrogen 5.82.

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## SECTION V.

*SUBSTANCES WHICH, SO FAR AS IS KNOWN, DO NOT BELONG TO EITHER OF THE PRECEDING SECTIONS.*

### *Colouring Matter.*

Infinite diversity exists in the colour of vegetable substances, but the prevailing tints are red, yellow, blue, and green, or mixtures of these colours. The colouring matter rarely or never occurs in an insulated state, but is always attached to some other proximate principle, such as mucilaginous, extractive, farinaceous, or resinous substances, by which some of its properties, and in particular that of solubility, is greatly influenced. Nearly all kinds of vegetable colouring matter are decomposed by the combined agency of the sun's rays and a moist atmosphere, and they are all, without exception, destroyed by chlorine. (Page 165.) Heat, likewise, has a similar effect, even without being very intense; for a temperature between 300° or 400° F. aided by moist air, destroys the colouring ingredient. Acids and alkalies commonly change the tint of vegetable colours, entering into combination with them, so as to form new compounds.

Several of the metallic oxides, and especially alumina, and the

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\* Quarterly Journal, vol. xiv. p. 436.

† Annals of Philosophy, N. S. vol. viii. p. 69.



oxides of iron and tin, form with colouring matter insoluble compounds, to which the name of *lakes* is applied. Lakes are commonly obtained by mixing alum or the muriate of the peroxide of tin with a coloured solution, and then by means of an alkali precipitating the oxide which unites with the colour at the moment of separation. On this property are founded many of the processes in dyeing and calico-printing. The art of the dyer consists in giving a uniform and permanent colour to cloth. This is sometimes effected merely by immersing the cloth in the coloured solution; whereas in other instances the affinity between the colour and the fibre of the cloth is so slight, that it only receives a stain which is removed by washing with water. In this case some third substance is requisite, which has an affinity both for the cloth and the colouring matter, and which, by combining at the same time with each, may cause the dye to be permanent. A substance of this kind was formerly called a *mordant*, but the term *basis*, introduced by the late Mr Henry of Manchester, is now more generally employed. The most important bases, and indeed the only ones in common use, are alumina, the oxide of iron, and the oxide of tin. The two former are exhibited in combination either with the sulphuric or acetic acid, and the latter most commonly as the muriate. Those colouring substances that adhere to the cloth without a basis are called *substantive* colours, and those which require a basis, *adjective* colours.

Various as are the tints observable in dyed stuffs, they may all be produced by the four simple ones, blue, red, yellow, and black; and hence it will be convenient to treat of colouring matters in that order.

*Blue dyes.*—Indigo is the chief substance employed for giving the blue dye. The best indigo is obtained from an American and Asiatic plant, the *Indigofera*, but an inferior sort has also been prepared from the *Isatis tinctoria* or *woad*, a native of Europe. The plant is cut a short time before its flowering, and is put into large vats covered with water, when fermentation spontaneously ensues, during which the indigo subsides in the form of a pulverulent pulpy matter. Its colour is at first green; but by exposure to the air it absorbs oxygen and becomes blue.

Indigo is a light brittle substance, of a deep blue colour, and without either taste or odour. At 550° F. it sublimes, forming a violet vapour with a tint of red, and condensing into long flat acicular crystals, which appear red by reflected, and blue by transmitted light. The process of subliming indigo is one of considerable delicacy, owing to the circumstance that the temperature at which it sublimes is very near that at which it is decomposed. Sublimation, however, affords the best method of procuring indigo in a state of perfect purity, and minute directions have been given by Mr Crum for conducting it with success. (An. of Phil. N. S. vol. v.)

Indigo in its dry state may be preserved without change; but when kept under water it is gradually decomposed. It is quite insoluble in water and alcohol, and is attacked by the alkalies in a partial manner. Its only proper solvent is concentrated sulphuric acid. When indigo is put into this acid, a yellow solution is at first formed, which, after a few hours, acquires a deep blue colour. If the indigo is pure, sulphurous acid is not generated, nor is the acid decomposed; but the indigo undergoes a change, for it is rendered soluble in water. To the indigo thus modified Mr Crum has applied the name of *cerulin*, and he regards it as a compound of one atom of indigo, and 4 atoms of water.

This solution, properly diluted with water, is employed by dyers for forming what is called the *Saxon blue*. Mr Crum has also described another compound of indigo and water, under the name of *Phenecin*, from *pourpre* purple, because it acquires a purple colour on the addition of a salt. It appears to consist of one atom of indigo, and two atoms of water.

When indigo, suspended in water, is brought into contact with certain deoxidizing agents, it is deprived of oxygen, becomes green, and is rendered soluble in water, and still more so in the alkalies. This effect is produced, for example, by sulphuretted hydrogen, by the hydrosulphuret of ammonia, by the protoxide of iron precipitated by lime or potassa, or by a solution of the sulphuret of arsenic in potash. On dipping cloth into a solution of deoxidized indigo, it receives a green tint, which becomes blue by exposure to the air. This is the usual method of dyeing blue by means of indigo, a colour which adheres permanently to cloth without the intervention of a basis.

From the analytical researches of Mr Crum, it appears that indigo is composed of nitrogen, oxygen, hydrogen, and carbon, in the proportion of 1 atom of the first element, 2 of the second, 4 of the third, and 16 of the fourth. This would make its atomic weight 130.

*Red dyes.*—The chief substances which are employed for giving the red dye are cochineal, archil, madder, Brazil wood, logwood, and safflower, all of which are adjective colours. The cochineal is obtained from an insect which feeds upon the leaves of several species of the *cactus*, and which is supposed to derive this colouring matter from its food. It is very soluble in water, and is fixed on cloth by means of alumina or the oxide of tin. Its natural colour is crimson; but when the bitartrate of potassa is added to the solution, it yields a rich scarlet dye. The beautiful pigment called *carmine* is a lake made of cochineal and alumina, or the oxide of tin.

The dye called *archil* is obtained from a peculiar kind of lichen, (*Lichen roccella*), which grows chiefly in the Canary Islands, and is employed by the Dutch in forming the blue pigment called *litmus* or *turnsol*. The colouring ingredient of litmus is a compound of the red colouring matter of the lichen and an alkali; and hence, on the addition of an acid, the colouring matter is set free, and the red tint of the plant is restored. Litmus is not only used as a dye, but is employed by chemists for detecting the presence of a free acid.

The colouring principle of logwood has been procured in a separate state by M. Chevreul, who has applied to it the name of *hematin*. (An. de. Ch. vol. lxxxi.) It is obtained in crystals by digesting the aqueous extract of logwood in alcohol, and allowing the alcoholic solution to evaporate spontaneously.

The safflower is the dried flowers of the *carthamus tinctorius*, which is cultivated in Egypt, Spain, and in some parts of the Levant. The pigment called *rouge* is prepared from this dye. Madder is the root of the *rubia tinctorum*.

*Yellow dyes.*—The chief yellow dyes are the quercitron bark, turmeric, wild American hiccory, fustic, and saffron. They are all adjective colours. The quercitron bark, which is one of the most important of the yellow dyes, was introduced into notice by Dr Bancroft. With a basis of alumina, the decoction of this bark gives a bright yellow dye. With the oxide of tin it communicates a variety of tints, which may be made to vary from a pale lemon colour to deep orange. With the oxide of iron it gives a drab colour.

Turmeric is the root of the *Curcuma longo*, a native of the East Indies. Paper stained with a decoction of this substance constitutes the *turmeric* or *curcuma* paper employed by chemists as a test of free alkali, by the action of which it receives a brown stain.

The colouring ingredient of saffron (*Crocus sativus*) is soluble in water and alcohol, has a bright yellow colour, is rendered blue and then lilac by sulphuric acid, and receives a green tint on the addition of nitric acid. From the great diversity of colours which it is capable of assuming under different circumstances, MM. Bouillon Lagrange and Vogel have proposed for it the name of *Polychroite*. (An. de Ch. vol. lxxx.)

*Black dyes.*—The black dye is made of the same ingredients as writing ink, and therefore consists essentially of a compound of the oxide of iron with gallic acid and tannin. From the addition of logwood and acetate of copper, the black receives a shade of blue.

By the dexterous combination of the four leading colours, blue, red, yellow, and black, all other shades of colour may be procured. Thus green is communicated by forming a blue ground with indigo, and then adding a yellow by means of quercitron bark.

The reader who is desirous of studying the details of dyeing and calico-printing, a subject which does not fall within the plan of this work, may consult Berthollet's *Elements de l'art de la Teinture*; the treatise of Dr Bancroft on Permanent Colours; a paper by Mr Henry in the third volume of the Manchester Memoirs; and the essay of Thénard and Roard in the 74th volume of the *Annales de Chimie*.

## Tannin.

Tannin exists in large quantity in the excrescences of several species of the oak, called *gall-nuts*; in the bark of most trees; in some inspissated juices, such as kino and catechu; in the leaves of the tea-plant, sumach, whortleberry, (*uva ursi*,) and in all astringent plants, being the chief cause of the astringency of vegetable matter. It is frequently associated with gallic acid, as for example, in gall-nuts, most kinds of bark, and in tea; but in kino, catechu, and cinchona bark, no gallic acid is present. In some instances tannin appears to be converted into gallic acid. Thus on exposing an infusion of gall-nuts for some time to the air, nearly all the tannin disappears, and a quantity of gallic acid is found in the liquid much greater than what it had originally contained. (Page 363.)

Several processes have been recommended for the preparation of tannin; but it is doubtful if it has ever, by these methods, been obtained in a pure state. Owing to this circumstance, the nature and composition of tannin is involved in obscurity. Proust proposes to prepare tannin by pouring the muriate of tin into a concentrated solution of Aleppo-galls, until the yellowish precipitate, which at first falls, ceases to appear. The precipitate is washed with a small quantity of cold water, and then dissolved in warm water, through which a current of sulphuretted hydrogen gas is transmitted, in order to precipitate the tin. From the clear liquid, after being filtered, the tannin, mixed with a little gallic acid and extractive matter, is procured by gentle evaporation.

Tannin, in its dry state, is a brown friable substance, of a resinous fracture, insoluble in pure alcohol, but soluble in water. The aqueous solution has a deep brown colour, and is said not to become

mouldy by keeping. It has a strong attraction both for acids and alkalies, forming compounds which are, for the most part, of sparing solubility in water. Thus the sulphuric, muriatic, and most other acids, added to a solution of gall-nuts, cause a precipitate, which is tannin combined with a portion of acid. The alkaline bases have a similar effect. Tannin is precipitated, for example, by the carbonates of potassa and ammonia, by the alkaline earths, by alumina, and many of the oxides of the common metals. Nitric acid and chlorine decompose tannin, producing a change, the nature of which is not well understood.

The most characteristic property of tannin is its action on a salt of iron and a solution of gelatine. With the peroxide of iron, or still better with the protoxide and peroxide mixed, tannin forms a black-coloured compound, which, together with the gallate of iron, constitutes the basis of writing ink, and the black dyes. (Page 363.) Mixed with a solution of gelatine, a yellowish flocculent precipitate subsides, which is insoluble in water, resists putrefaction powerfully, and on drying becomes hard and tough. This substance, to which the name of *tanno-gelatine* has been applied, is the essential basis of leather, being always formed when skins are macerated in an infusion of bark. The composition of *tanno-gelatine* is not always uniform, having been found by Dr Duncan, jun. and Dr Bostock, to vary with the proportions employed. If the gelatine is added in slight excess only, the resulting compound consists, according to Sir H. Davy, of 54 parts of gelatine and 46 of tannin; so that the quantity of tannin contained in any fluid may in this way be determined with tolerable precision. *Tanno-gelatine* is soluble to a considerable extent in an excess of gelatine.

From an analysis of the compound of tannin and the oxide of lead, Berzelius states that 100 parts of tannin are composed of carbon 50.55, oxygen 45, and hydrogen 4.45. Little reliance, however, can be placed on this result, because we are quite uncertain as to the purity of the tannin, which was combined with the lead.

From the experiments of Sir H. Davy, it appears that the inner cortical layers of barks are the richest in tannin. The quantity is greatest in the beginning of spring, at the time the buds begin to open, and smallest during winter. Of all the varieties of bark which he examined, that of the oak contains the greatest quantity of tannin.

*Artificial tannin.*—This interesting substance was discovered twenty years ago by Mr Hatchett, who gave a full description of it in the Philosophical Transactions for 1805 and 1806. The best method of preparing it, is by the action of nitric acid on charcoal. For this purpose, 100 grains of charcoal in fine powder are digested in nitric acid, of density 1.4, diluted with two ounces of water. The mixture is exposed to a gentle heat, which is to be continued until all the charcoal is dissolved. The reddish-brown solution is then evaporated to dryness, in order to expel the pure acid, the temperature being carefully regulated towards the close of the process, so that the product may not be decomposed.

Artificial tannin is a brown fusible substance, of a resinous fracture, and astringent taste. It is soluble even in cold water and alcohol. It reddens litmus paper, probably from adhering nitric acid. With a salt of iron and solution of gelatine it acts precisely in the same manner as natural tannin. It differs, however, from that substance in not being decomposed by the action of strong nitric acid.

Artificial tannin may be prepared in several ways. Thus it is generated by the action of nitric acid, both on animal or vegetable charcoal, and on pit-coal, asphaltum, jet, indigo, common resin, and several resinous substances. It is also procured by treating common resin, elemi, asafoetida, camphor, balsams, &c. first with sulphuric acid, and then with alcohol.

### *Gluten.—Yeast.—Vegetable Albumen.*

Gluten is procured by the process which was described for preparing starch from wheat flour. (Pages 388, 389.) It has a gray colour and fibrous structure, accompanied with a high degree of viscosity and elasticity. It has scarcely any taste, and is insoluble in water, alcohol, and ether; but Dr Bostock found, that a small portion is taken up by long digestion in water. Both the acids and alkalies dissolve gluten. The acid solution is precipitated by an alkali, and reciprocally the alkaline solution by an acid, the gluten in each case having lost its elasticity.

When gluten is kept in a warm moist situation, it ferments, and an acid is formed; but in a few days putrefaction ensues, and an offensive odour, like that of putrefying animal matter, is emitted. According to Proust, who has made these spontaneous changes a particular object of study, the process is divisible into two distinct periods. In the first, carbonic acid and pure hydrogen gases are evolved; and in the second, besides the acetic and phosphoric acids and ammonia, two new compounds are generated, for which he proposes the name of *caseic acid* and *caseous oxide*. These are the same principles which are generated during the fermentation of the curd of milk, and to the former is owing the characteristic flavour of cheese. It is apparent from these circumstances that gluten contains nitrogen as one of its elements, and that it approaches closely to the nature of animal substances. It has hence been called a *vegeto-animal principle*.

If gluten is dried by a gentle heat, it contracts in volume, becomes hard and brittle, and may in this state be preserved without change. Exposed to a strong heat, it yields, in addition to the usual inflammable gases, a thick fetid oil, and carbonate of ammonia.

Gluten is present in most kinds of grain, such as wheat, barley, rye, oats, peas, and beans; but the first contains it in by far the largest proportion. This is the reason that wheaten bread is more nutritious than that made with other kinds of flour; for of all vegetable substances gluten appears to be the most nutritive. It is to the presence of gluten that wheat-flour owes its property of forming a tenacious paste with water. To the same cause is owing the formation of light spongy bread, the carbonic acid which is disengaged during the fermentation of dough, being detained by the viscid gluten, distends the whole mass, and thus produces the *rising* of the dough. From the experiments of Sir H. Davy, it appears that good wheat flour contains from 19 to 24 per cent. of gluten. The wheat grown in the south of Europe is richer in gluten than that of colder climates.

M. Taddey, an Italian chemist, has succeeded in obtaining two distinct principles from gluten, to one of which he has applied the name of *gliadine*, from  $\gamma λ ι α$  *gluten*, and to the other that of *zymome*, from  $ζ υ μ η$ , a ferment. (Ann. of Phil. vol. xv.)

To obtain these principles, the gluten is boiled with successive portions of alcohol, until the spirit ceases to be rendered milky by the ad-



dition of water. By this process the gliadine, which is soluble in alcohol, is dissolved, and may be procured by evaporating the alcoholic solution, while the zymome, which is insoluble in that menstruum, is left in a pure state.

Gliadine is a brittle, slightly transparent substance, of a yellow colour, and a sweetish balsamic taste. Its smell, in the cold, is like that of the honeycomb; but, when heated, it emits an odour similar to that of boiled apples. It is soluble to a considerable extent in boiling alcohol, and is in part deposited in cooling. The alcoholic solution is rendered milky by water, and the gliadine is precipitated in white flakes by alkaline carbonates. It is insoluble in water, but is dissolved by acids and alkalies. When heated in the open air, it takes fire, and burns with a bright flame.

Zymome is a hard tough substance, but does not possess the viscosity of gluten. It is insoluble in water and alcohol; but it is dissolved in vinegar and the mineral acids by the aid of heat, and forms a soap with pure potassa. Under favourable circumstances it putrefies, without previously fermenting like gluten; and when heated it emits an odour like that of burning hair. It produces various kinds of fermentation according to the nature of the substance with which it comes in contact.

M. Taddey has discovered a very delicate test of the presence of Zymome. On mixing the powder of guaiacum with zymome, a beautiful blue colour instantly appears, and the same phenomenon ensues, though less rapidly, when it is kneaded with gluten or the flour of good wheat moistened with water. With bad flour, the gluten of which has suffered spontaneous decomposition, the blue tint is scarcely visible. The intensity of the colour, indeed, is entirely dependent on the relative quantity of zymome contained in the flour; and since the quantity of zymome is proportional to the quantity of gluten, the proportion of the latter, and therefore the quality of the flour, may be estimated approximately by the action of guaiacum.

The nature of the change which gives rise to the blue colour has not been explained; but oxygen gas is obviously essential to it, since the phenomenon does not take place at all when atmospheric air is excluded.

*Yeast.*—This substance is always generated during the vinous fermentation of vegetable juices and decoctions, rising to the surface in the form of a frothy, flocculent, somewhat viscid matter, the nature and composition of which are unknown. It is insoluble in water and alcohol, and in a warm moist atmosphere gradually putrefies, a sufficient proof that ammonia is one of its elements. Submitted to a moderate heat, it becomes dry and hard, and may in this state be preserved without change. Heated to redness in close vessels, it yields products similar to those procured under the same circumstance from gluten. To this substance, indeed, yeast is supposed by some chemists to be very closely allied.

The most remarkable property of yeast is that of exciting fermentation. By exposure for a few minutes to the heat of boiling water, it loses this property, but after some time again acquires it. Nothing conclusive is known concerning either the nature of these changes, or the mode in which yeast operates in establishing the fermentative process.

*Vegetable albumen.*—Some vegetables contain a substance coagulable by heat, and which is very analogous to animal albumen or curd.

It was found in the bitter almond by Vogel, in the sweet almond by M. Boullay, and probably exists in most of the emulsive seeds. (Ann. of Ph. vol. xii. p. 39.)

*Asparagin, Bassorin, Caffein, Cathartin, Fungin, Suberin, Ulmin, Lupulin, Inulin, Medullin, Pollenin, Piperin, Olivile, Sarcocoll, Extractive Matter, Bitter Principle, &c.*

*Asparagin*.—This principle was discovered by MM. Vauquelin and Robiquet in the juice of the asparagus, from which it is deposited in crystals by evaporation. Its taste is cool and slightly nauseous, it is soluble in water, and has neither an acid nor alkaline reaction. (Ann. de Ch. vol. lvii.)

*Bassorin* was first noticed in gum *Bassora* by Vauquelin. According to Gehlen and Bucholz, it is contained, together with common gum, in the gum tragacanth, and John found it in the gum of the cherry tree. Salep, from the experiments of Caventou, appears to consist almost totally of Bassorin.

Bassorin is characterized by forming with cold water a bulky jelly which is insoluble in that menstruum, as well as in alcohol and ether. Boiling water does not dissolve it except by long continued ebullition, when the bassorin at length disappears, and is converted into a substance similar to gum arabic.

*Caffein* was discovered in coffee by M. Robiquet in the year 1821, and was soon after obtained from the same source by Pelletier and Caventou, without a knowledge of the discovery of Robiquet. It is a white crystalline volatile matter, which is soluble in boiling water and alcohol, and is deposited on cooling in the form of silky filaments like amianthus. M. Pelletier, contrary to the opinion of M. Robiquet, at first regarded it as an alkaline base; but he now admits that it does not affect the vegetable blue colours, nor combine with acids. (Journal de Pharmacie for May 1826.)

Hitherto the properties of Caffein have not been fully described. From the analysis of Pelletier and Dumas, 100 parts of it consist of carbon 46.51, nitrogen 21.54, hydrogen 4.81, and oxygen 27.14. Though it contains more nitrogen than most animal substances, it does not, under any circumstances, undergo the putrefactive fermentation.

*Cathartin*.—This name has been applied by MM. Lassaigue and Feneulle to the active principle of senna. (An. de Ch. et de Ph. vol. xvi.)

*Fungin*.—This name is applied by M. Braconnot to the fleshy substance of the mushroom, and is procured in a pure state by digestion in hot water, to which a little alkali is added. Fungin is nutritious in a high degree, and in composition is very analogous to animal substances. Like flesh, it yields nitrogen gas when digested in dilute nitric acid.

*Suberin*.—This name has been applied by M. Chevreul to the cellular tissue of the common cork, the outer bark of the cork-oak, (*quercus suber*,) after the astringent, oily, resinous, and other soluble matters have been removed by the action of water and alcohol. Suberin differs from all other vegetable principles by yielding the suberic when treated by nitric acid.

*Ulmin*, discovered by Klapproth, is a substance which exudes spon-

taneously from the elm, oak, chesnut, and other trees; and according to Berzelius is a constituent of most kinds of bark. It may be prepared by acting upon elm-bark by hot alcohol, and cold water, and then digesting the residue in water which contains an alkaline carbonate in solution. On neutralizing the alkali with an acid, the ulmin is precipitated.

Ulmin is a dark brown, nearly black substance, is insipid and inodorous, and is very sparingly soluble in water and alcohol. It dissolves freely, on the contrary, in the solution of an alkaline carbonate, and is thrown down by an acid.

*Lupulin* is the name applied by Dr Ives to the active principle of the hop, but which has not yet been obtained in a state of purity.

*Inulin* is a white powder like starch, which is spontaneously deposited from a decoction of the roots of the *Inula helenium* or *Elecampane*. This substance is insoluble in cold, and soluble in hot water, and is deposited from the latter as it cools, a character which distinguishes it from starch. With iodine it forms a greenish-yellow compound of a perishable nature. Its solution is somewhat mucilaginous; but inulin is distinguished from gum by insolubility in cold water, and in not yielding the saccholactic when digested in nitric acid.

*Medullin*.—This name was applied by John to the pith of the sunflower, but its existence as an independent principle is somewhat dubious. The term *pollenin* has been given by the same chemist to the pollen of tulips.

*Piperin* is the name which is applied to a white crystalline substance extracted from black pepper. It is tasteless, and is quite free from pungency, the stimulating property of the pepper being found to reside in a fixed oil. (Pelletier, in An. de Ch. et de Ph. vol. xvi.)

*Olivile*.—When the gum of the olive tree is dissolved in alcohol, and the solution is allowed to evaporate spontaneously, a peculiar substance, apparently different from the other proximate principles hitherto examined, is deposited either in flattened needles or as a brilliant amylaceous powder. To this M. Pelletier, its discoverer, has given the name of *Olivile*. (An. of Phil. vol. xii.)

*Sarcocoll* is the concrete juice of the *Penæa sarcocolla*, a plant which grows in the northern parts of Africa. It is imported in the form of small grains of a yellowish or reddish colour like gum arabic, to which its properties are similar. It has a sweetish taste, dissolves in the mouth like gum, and forms a mucilage with water. It is distinguished from gum, however, by its solubility in alcohol, and by its aqueous solution being precipitated by tannin. Dr Thomson, who has given a full account of sarcocoll in his System of Chemistry, considers it closely allied to the saccharine matter of liquorice.

*Rhubarbarin* is the name employed by Pfaff to designate the principle in which the purgative property of the rhubarb resides. M. Nani of Milan regards the active principle of this plant as a vegetable alkali; but he has not given any proof of its alkaline nature. (Journal of Science, vol. xvi. page 172.)

*Colocynthin*.—This name is applied by Vauquelin to a bitter resinous matter extracted from colocynth, and to which he ascribes the properties of this substance. (Journal of Science, vol. xviii. page 400.)

*Bitter Principle*.—This name was formerly applied to a substance supposed to be common to bitter plants, and to be the cause of their peculiar taste. The recent discoveries in vegetable chemistry, however, have shown that it can no longer be regarded as a uniform un-

varying principle. The bitterness of the *nux vomica*, for example, is owing to strychnia, that of opium to morphia, that of cinchona bark to cinchonia and quinia, &c. The cause of the bitter taste in the root of the squill is different from that of the hop or of gentian. The term bitter principle should therefore be abandoned.

*Extractive Matter.*—This expression, if applied to one determinate principle supposed to be the same in different plants, is not less vague than the foregoing. It is indeed true that most plants yield to water a substance which differs from gum, sugar, or any proximate principle of vegetables, which therefore constitutes a part of what is called an *extract* in pharmacy, and which, for want of a more precise term, may be expressed by the name of *extractive*. It must be remembered, however, that this matter is always mixed with other proximate principles, and that there is no proof whatever of its being identical in different plants. The solution of saffron in hot water, said to afford pure extractive matter by evaporation, contains the colouring matter of the plant, (page 395,) together with all the other vegetable principles of saffron, which happen to be soluble in the menstruum employed.

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## SECTION VI.

### ON THE SPONTANEOUS CHANGES OF VEGETABLE MATTER.

Vegetable substances, for reasons already explained in the remarks introductory to the study of organic chemistry, are very liable to spontaneous decomposition. So long, indeed, as they remain in connexion with the living plant by which they were produced, the tendency of their elements to form new combinations is controlled; but as soon as the vital principle is extinct, of the agency of which no satisfactory explanation can at present be afforded, they become subject to the unrestrained influence of chemical affinity. To the spontaneous changes which they then experience from the operation of this power, the term *fermentation* is applied.

As might be expected from the difference in the constitution of different vegetable compounds, they are not all equally prone to fermentation; nor is the nature of the change the same in all of them. Thus alcohol, oxalic, acetic, and benzoic acids, probably the vegetable alkalies, and pure naphtha, may be kept for years without change, and some of them appear unalterable; while others, such as gluten, sugar, starch, and mucilaginous substances, are very liable to decomposition. In like manner, the spontaneous change sometimes terminates in the formation of sugar, at another time in that of alcohol, at a third, in that of acetic acid, and at a fourth, in the total dissolution of the substance. This has led to the division of the fermentative processes into four distinct kinds, namely, the *saccharine*, the *vinous*, the *acetous*, and the *putrefactive* fermentation.

#### *Saccharine Fermentation.*

The only substance known to be subject to the first kind of fermentation is starch. When gelatinous starch, or amidine, is kept in a

moist state for a considerable length of time, a change gradually ensues, and a quantity of sugar, equal to about half the weight of the starch employed, is generated. (Page 390.) Exposure to the atmosphere is not necessary to this change, but the quantity of sugar is increased by the excess of air.

The germination of seeds, as exemplified in the malting of barley, is likewise an instance of the saccharine fermentation; but as it differs in some respects from the process above mentioned, being probably modified by the vitality of the germ, it may with greater propriety be discussed in the following section.

The ripening of fruit has also been regarded as an example of the saccharine fermentation, especially since some fruits, such as the pear and apple, if gathered before their maturity, become sweeter by keeping. I cannot, however, adopt this opinion. The process of ripening appears to consist in the conversion, not of starch, but of acid into sugar. Such at least is the view deducible from the experiments of Proust, who examined the unripe grape in its different stages towards maturity. He found that the green fruit contains a large quantity of free acid, chiefly the citric, which, as the grape ripens, gradually disappears, while its place is occupied by sugar. It is hence probable that the elements of the acid itself, as the result of a vital process, are made to enter into a new arrangement, by which sugar is generated. The formation of an acid may be regarded as one step towards the production of saccharine matter, a view which will account for the strong acidity of many fruits, such as the gooseberry and currant, just before they begin to ripen.

### *Vinous Fermentation.*

The conditions which are required for establishing the vinous fermentation are four in number, namely, the presence of sugar, water, yeast, and a certain temperature. The best mode of studying this process, so as to observe the phenomena, and determine the nature of the change, is to place five parts of sugar, with about twenty of water, in a glass flask furnished with a bent tube, the extremity of which opens under an inverted jar full of water or mercury; and after adding a little yeast, to expose the mixture to a temperature of about 60° or 70° Fahr. In a short time bubbles of gas begin to collect in the vicinity of the yeast, and the liquid is soon put into brisk motion, in consequence of the formation and disengagement of a large quantity of gaseous matter; the solution becomes turbid, its temperature rises, and froth collects upon the surface. After continuing for a few days, the evolution of gas begins to abate, and at length ceases altogether; the impurities gradually subside, and leave the liquor clear and transparent.

The only appreciable changes which are found to have occurred during the process, are the disappearance of the sugar, and the formation of alcohol, which remains in the flask, and of carbonic acid gas, which is collected in the pneumatic apparatus. A small portion of yeast is decomposed; but the quantity is so minute that it may without inconvenience be left out of consideration. The yeast indeed appears to operate only in exciting the fermentation, without further contributing to the products. The atmospheric air, it is obvious, has no share in the phenomena, since it may be altogether excluded without affecting the result. The theory of the process is founded on the



fact that the sugar, which disappears, is almost precisely equal to the united weights of the alcohol and carbonic acid ; and hence the former is supposed to be resolved into the two latter. The mode in which this change is conceived to take place has been ably explained by Gay-Lussac, an explanation which will easily be understood by comparing the composition of sugar with that of alcohol. The elements of sugar, which consist of carbon, hydrogen, and oxygen, in the ratio of one atom of each, (page 388) are multiplied by three, in order to equalize the quantity of hydrogen contained in the two compounds. (An. de Ch. tome xcv. p. 317.)

<i>By Weight.</i>		<i>Alcohol.</i>	<i>By Volume.</i>	
<i>Sugar.</i>			<i>Sugar.</i>	<i>Alcohol.</i>
Carbon, 18 or 3 atoms.	12 or 2 atoms.	Vapour of } Carbon, } Hydrogen, } Oxygen, }	3	2
Hydrogen, 3 or 3 atoms.	3 or 3 atoms.		3	3
Oxygen. 24 or 3 atoms.	8 or 1 atom.		$\frac{3}{2}$	$\frac{1}{2}$
<hr/> 45	<hr/> 23			

Now on inspecting this table, and remembering that carbonic acid consists of one atom of carbon, or one volume of its vapour, and two atoms or one volume of oxygen, it will be apparent that the elements of sugar are in such proportion as to form one atom of alcohol, or one volume of its vapour, and one atom or one volume of carbonic acid. Therefore 45 parts of sugar are capable of furnishing 23 of alcohol and 22 parts of carbonic acid.

It admits of doubt whether any substance besides sugar is capable of undergoing the vinous fermentation. The only other principle which is supposed to possess this property is starch, and this opinion chiefly rests on the two following facts. First, It is well known that potatoes, which contain but little sugar, yield a large quantity of alcohol by fermentation, during which the starch disappears. And, secondly, M. Clement procured the same quantity of alcohol from equal weights of malted and unmalted barley\*. Nothing conclusive can be inferred, however, from these data; for, from the facility with which starch is converted into sugar it is probable that the saccharine may precede the vinous fermentation.

Though a solution of pure sugar is not susceptible of the vinous fermentation without being mixed with yeast, yet the saccharine juices of plants do not require the addition of that substance, or in other words, they contain some principle, which, like yeast, excites the fermentative process. Thus must or the juice of the grape ferments spontaneously; but Gay-Lussac has observed that these juices cannot begin to ferment unless they are exposed to the air. By heating must to 212° F., and then corking it carefully, the juice may be preserved without change; but if it be exposed to the air for a few seconds only, it absorbs oxygen, and fermentation takes place. From this it would appear that the must contains a principle which is convertible into yeast, or at least acquires the characteristic property of that substance, by absorbing oxygen.

The various kinds of stimulating fluids, prepared by means of the vinous fermentation, are divisible into wines which are formed from the

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\* An. de Chimie et de Physique, tome v. p. 422.

juices of saccharine fruits, and the various kinds of ale and beer produced from a decoction of the nutritive grains previously malted.

The juice of the grape is superior, for the purpose of making wine, to that of all other fruits, not merely in containing a larger proportion of saccharine matter, since this deficiency may be supplied artificially, but in the nature of its acid. The chief or only acidulous principle of the mature grape, ripened in a warm climate, such as Spain, Portugal, or Madeira, is the bitartrate of potassa. As this salt is insoluble in alcohol, the greater part of it is deposited during the vinous fermentation; and an additional quantity subsides, constituting the *crust*, during the progress of wine towards its point of highest perfection. The juices of other fruits, on the contrary, such as the gooseberry or currant, contain the malic and citric acids, which are soluble both in water and alcohol, and of which therefore they can never be deprived. Consequently these wines are only rendered palatable by the presence of free sugar, which conceals the taste of the acid; and hence it is necessary to arrest the progress of the fermentation long before the whole of the saccharine matter is consumed. For the same reason, these wines do not admit of being long kept; for as soon as the free sugar is converted into alcohol by the slow fermentative process, which may be retarded by the addition of brandy, but cannot be prevented, the wine acquires a strong sour taste.

Ale and beer differ from wines in containing a large quantity of mucilaginous and extractive matters derived from the malt with which they are made. From the presence of these substances they always contain a free acid, and are greatly disposed to pass into the acetous fermentation. The sour taste is concealed partly by free sugar, and partly by the bitter flavour of the hop, the presence of which diminishes the tendency to the formation of an acid.

The fermentative process which takes place in dough mixed with yeast, and on which depends the formation of good bread, has been supposed to be of a peculiar kind, and is sometimes designated by the name of *panary fermentation*. The late ingenious researches of Dr Colquhoun, however, leave little or no doubt that the phenomena are to be ascribed to the saccharine matter of the flour undergoing the vinous fermentation, by which it is resolved into alcohol and carbonic acid. (Edinburgh Journal of Science, vol. vi.)

### *Acetous Fermentation.*

When any liquid which has undergone the vinous fermentation, or even pure alcohol diluted with water, is mixed with yeast, and exposed in a warm place to the open air, an intestine movement speedily commences, heat is developed, the fluid becomes turbid from the deposition of a peculiar filamentous matter, oxygen is absorbed from the atmosphere, and carbonic acid is disengaged. These changes, after continuing a certain time, cease spontaneously; the liquor becomes clear, and instead of alcohol, it is now found to contain acetic acid. This process is called the *acetous fermentation*.

The vinous may easily be made to terminate in the acetous fermentation; nay, the transition takes place so easily, that in many instances, in which it is important to prevent it, this is with difficulty effected. It is the uniform result if the fermenting liquid be exposed to a warm temperature and to the open air; and the means by which it is avoided is by excluding the atmosphere, or by exposure to cold.

For the acetous fermentation a certain degree of warmth is indispensable. It takes place tardily below 60° F; at 50° it is very sluggish; and at 32°, or not quite so low, it is wholly arrested. It proceeds with vigour, on the contrary, when the thermometer ranges between 60° and 80°, and is even promoted by a temperature somewhat higher. The presence of water is likewise essential; and a portion of yeast, or some analogous substance, by which the process may be established, must also be present.

The information contained in chemical works relative to the substances susceptible of the acetous fermentation is somewhat confused, a circumstance which appears to have arisen from phenomena of a totally different nature being included under the same name. It seems necessary to distinguish between the mere formation of acetic acid, and the acetous fermentation. Several or perhaps most vegetable substances yield acetic acid when they undergo spontaneous decomposition. Mucilaginous substances in particular, though excluded from the air, gradually become sour; and consistently with this fact, inferior kinds of ale and beer are known to acquire acidity in a short time, even when confined in well-corked bottles. In like manner, a solution of sugar, mixed with water in which the gluten of wheat has fermented, and kept in close vessels, was found by Fourcroy and Vauquelin to yield acetic acid. All these processes, however, appear essentially different from the proper acetous fermentation above described, being unattended with visible movement in the liquid, with absorption of oxygen, or disengagement of carbonic acid.

The acetous fermentation, in this limited sense, consists in the conversion of alcohol into acetic acid. That this change does really take place is inferred, not only from the disappearance of alcohol and the simultaneous production of acetic acid, but also from the quantity of the latter being precisely proportional to that of the former. The nature of the chemical action, however, is at present exceedingly obscure. Indeed the only probable explanation which has been offered is the following. Since alcohol contains a greater proportional quantity of carbon and hydrogen than acetic acid, it has been supposed that the oxygen of the atmosphere, the presence of which is indispensable, abstracts so much of those elements, by giving rise to the formation of carbonic acid and water, as to leave the remaining carbon, hydrogen and oxygen of the alcohol in the precise ratio for forming acetic acid. The experiments of Saussure, however, are incompatible with this view. According to his researches, the quantity of carbonic acid generated during the acetous fermentation is precisely equal in volume to the oxygen which is absorbed; and hence it is inferred, that this gas unites exclusively with the carbon of the alcohol. This result is different from what might have been anticipated, and requires confirmation.

The acetous fermentation is conducted on a large scale for yielding the common vinegar of commerce. In France it is prepared by exposing weak wines to the air during warm weather; and in this country it is made from a solution of brown sugar or molasses, or an infusion of malt. The vinegar thus obtained always contains a large quantity of mucilaginous and other vegetable matters, the presence of which renders it liable to several ulterior changes.

### *Putrefactive Fermentation.*

By this term is implied a process which is not attended with the

phenomena of the saccharine, vinous, or acetous fermentation, but during which the vegetable matter is completely decomposed. All proximate principles are not equally liable to this kind of dissolution. Those in which charcoal and hydrogen prevail, such as the oils, resins, and alcohol, do not undergo the putrefactive fermentation; nor do acids, which contain a considerable excess of oxygen, manifest a tendency to suffer this change. Those substances alone are disposed to putrefy, the oxygen and hydrogen of which are in proportion to form water; and such, in particular, as contain nitrogen. Among these, however, a singular difference is observable. Caffein evinces no tendency to spontaneous decomposition, while gluten, which certainly must contain a less proportional quantity of nitrogen, putrefies with great facility. It is difficult to assign the precise cause of this difference; but it most probably depends partly upon the mode in which the ultimate elements of bodies are ranged, and partly on their cohesive power;—those substances, the texture of which is the most loose and soft, being, *cæteris paribus*, the most liable to spontaneous decomposition.

The conditions which are required for enabling the putrefactive process to take place, are moisture, air, and a certain temperature.

The presence of a certain degree of moisture is absolutely necessary; and hence vegetable substances, which are disposed to putrefy under favourable circumstances, may be preserved for an indefinite period if carefully dried, and protected from humidity. Water acts apparently by softening the texture, and thus counteracting the agency of cohesion; and a part of the effect may also be owing to its affinity for some of the products of the putrefaction. It is not likely that this liquid is actually decomposed, since water appears to be a uniform product.

The air cannot be regarded as absolutely necessary, since putrefaction is found to be produced by the concurrence of the two other conditions only; but the process is without doubt materially promoted by free exposure to the atmosphere. Its operation is of course attributable to the oxygen combining with the carbon and hydrogen of the decaying substance.

The temperature most favourable to the putrefactive process is between 60° and 100° Fahr. A strong heat is unfavourable, by expelling moisture; and a cold of 32° F. at which water congeals, arrests its progress altogether. The mode in which caloric acts is the same as in all similar cases, namely, by tending to separate elements from one another which are already combined.

The products of the putrefactive fermentation may be divided into the solid, liquid and gaseous. The liquid are chiefly water, together with a little acetic acid, and probably oil. The gaseous products are light carburetted hydrogen, carbonic acid, and, when nitrogen is present, ammonia. Pure hydrogen, and probably nitrogen, are sometimes disengaged. Thus hydrogen and carbonic acid, according to Proust, are evolved from putrefying gluten; and Saussure obtained the same gases from the putrefaction of wood in close vessels. Under ordinary circumstances, however, the chief gaseous product of decaying plants is light carburetted hydrogen, which is generated in great quantity at the bottom of stagnant pools during summer and autumn. (Page 191.) Another elastic principle, supposed to arise from putrefying vegetable remains, is the noxious miasm of marshes. The origin of these miasms, however, is exceedingly obscure. Every attempt to obtain them in an insulated state has hitherto proved abortive; and

therefore, if they are really a distinct species of matter, they must be regarded, like the effluvia of contagious fevers, as of too subtile a nature for being subjected to chemical analysis.

When the decay of leaves or other parts of plants has proceeded so far that all trace of organization is effaced, a dark pulverulent substance remains, consisting of charcoal combined with a little oxygen and hydrogen. This compound is vegetable mould, which, when mixed with a proper quantity of earth, constitutes the soil necessary to the growth of plants. Saussure, in his excellent *Recherches Chimiques sur la Végétation*, has described vegetable mould as a substance of uniform composition; and on heating it to redness in close vessels, he procured carburetted hydrogen and carbonic acid gases, water holding the acetate or carbonate of ammonia in solution, a minute quantity of empyreumatic oil, and a large residue of charcoal mixed with saline and earthy ingredients. On exposing vegetable mould to the action of light, air, and moisture, a chemical change ensues, the effect of which is to render a portion of it soluble in water, and thus applicable to the nutrition and growth of plants.

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## SECTION VII.

### ON THE CHEMICAL PHENOMENA OF GERMINATION AND VEGETATION.

#### Germination.

Germination is the process by which a new plant originates from seed. A seed consists essentially of two parts, the *Germ* of the future plant, endowed with a principle of vitality, and the *Cotyledons* or *Seed-lobes*, both of which are enveloped in a common covering of cuticle. In the germ two parts, the *radicle* and *plumula*, may be distinguished, the former of which is destined to descend into the earth and constitute the root, the latter to rise into the air and form the stem of the plant. The office of the seed-lobes is to afford nourishment to the young plant until its organization is so far advanced, that it may draw materials for its growth from extraneous sources. For this reason seeds are composed of highly nutritious ingredients. The chief constituent of most of them is starch, in addition to which they frequently contain gluten, gum, vegetable albumen or cuit, and sugar.

The conditions necessary to germination are three-fold; namely, moisture, a certain temperature, and the presence of oxygen gas. The necessity of moisture to this process has been proved by extensive observation. It is well known that the concurrence of other conditions cannot enable seeds to germinate, provided they are kept quite dry.

A certain degree of warmth is not less essential than moisture. Germination cannot take place at 32° F.; and a strong heat, such as that of boiling water, prevents it altogether, by depriving the germ of the vital principle. The most favourable temperature ranges from 60° to 80°, the precise degree varying with the nature of the plant, a circum-



stance that accounts for the difference in the season of the year at which different seeds begin to germinate.

That the presence of air is necessary to germination was demonstrated by several philosophers, such as Ray, Boyle, Muschenbroek and Boerhaave, before the chemical nature of the atmosphere was discovered; and Scheele, soon after the discovery of oxygen, proved that beans do not germinate without exposure to that gas. Achard afterwards demonstrated the same fact with respect to seeds in general, and his experiments have been fully confirmed by subsequent observers. It has even been shown by Humboldt, that a dilute solution of chlorine, owing to the tendency of that gas to decompose water and set oxygen at liberty, promotes the germination of seeds. These circumstances account for the fact that seeds, when buried deep in the earth, are unable to germinate.

It is remarkable that the influence of light, which is so favourable to all the subsequent stages of vegetation, is injurious to the process of germination. Ingenhousz and Sennebier have proved that a seed germinates more rapidly in the shade than in light, and in diffused day-light quicker than when exposed to the direct solar rays.

From the preceding remarks it is apparent that when a seed is placed an inch or two under the surface of the ground in spring, and is loosely covered with earth, it is in a state every way conducive to germination. The ground is warmed by absorbing the solar rays, and is moistened by occasional showers; the earth at the same time protects the seed from light, but by its porosity gives free access to the air.

The operation of malting barley, in which the grain is made to germinate by exposure to warmth, air, and humidity, affords the best means of studying the phenomena of germination. In this process, water is absorbed, the cotyledon swells and ruptures its cuticle, and soon after the radicle and plumula are protruded. On examining the grain at this period, it is found to have undergone an essential change in the proportion of its ingredients, as appears from the result of Proust's comparative analysis of malted and unmalted barley. (*An. de. Ch. et de Ph. tome v.*)

	<i>In 100 parts of Barley.</i>	<i>In 100 parts of Malt.</i>
Resin,	1	1
Gum,	4	15
Sugar,	5	15
Gluten,	3	1
Starch,	32	56
Hordein,	55	12

It is hence apparent that in germination the hordein is converted into starch, gum, and sugar; so that from an insoluble material, which could not in that state be applied to the uses of the young plant, two soluble and highly nutritive principles result, which by being dissolved in water are readily absorbed by the radicle.

The chemical changes which take place in germination have been ably investigated by Saussure, whose experiments are detailed in the work to which I have already referred. The leading facts which he determined are the following;—that oxygen gas is consumed, that carbonic acid is evolved, and that the volume of the latter is precisely equal to that of the former. Now since carbonic acid gas contains its own volume of oxygen, it follows that this gas must have united exclusively with carbon. It is likewise obvious that the grain must weigh less after than before germination, provided it is brought

to the same state of dryness in both instances. Saussure indeed found that the loss is greater than can be accounted for by the carbon of the carbonic acid which is evolved, and hence he concluded that a portion of water, generated at the expense of the grain itself, is dissipated in drying. According to Proust, the diminution in weight is about a third; but Dr Thomson affirms that in 50 processes, conducted on a large scale under his inspection, the average loss did not exceed one-fifth.

### *On the Growth of Plants.*

While a plant differs from an animal in exhibiting no signs of perception or voluntary motion, and in possessing no stomach to serve as a receptacle for its food, there exists between them a close analogy both of parts and functions, which, though not discerned at first, becomes striking on a near examination. The stem and branches act as a frame work or skeleton for the support and protection of the parts necessary to the life of the individual. The root serves the purpose of a stomach by imbibing nutritious juices from the soil, and thus supplying the plant with materials for its growth. The sap or circulating fluid, composed of water holding in solution saline, extractive, mucilaginous, saccharine, and other soluble substances, rises upwards through the wood in a distinct system of tubes called the *common vessels*, which correspond in their office to the lacteals and pulmonary arteries of animals, and are distributed in minute ramifications over the surface of the leaves. In its passage through this organ, which may be termed the lungs of a plant, the sap is fully exposed to the agency of light and air, experiences a change by which it is more completely adapted to the wants of the vegetable economy, and then descends through the inner layer of the bark in another system of tubes called the *proper vessels*, yielding in its course all the juices and principles peculiar to the plant.

The chemical changes which take place during the circulation of the sap are in general of such a complicated nature, and so much under the control of the vital principle, as to elude the sagacity of the chemist. One part of the subject, however, namely the reciprocal agency of the atmosphere and growing vegetables on each other, falls within the reach of chemical inquiry, and has accordingly been investigated by several philosophers.

For the leading facts relative to what is called the *respiration* of plants, or the chemical changes which the leaves of growing vegetables produce on the atmosphere, we are indebted to Priestley and Ingenhousz, the former of whom discovered that plants absorb carbonic acid from the air under certain circumstances, and emit oxygen in return; and the latter ascertained that this change occurs only during exposure to the direct rays of the sun. When a healthy plant, the roots of which are supplied with proper nourishment, is exposed to the direct solar beams in a given quantity of atmospheric air, the carbonic acid after a certain interval is removed, and an equal volume of oxygen is substituted for it. If a fresh portion of carbonic acid is supplied, the same result will ensue. In like manner, Sennebier and Woodhouse observed, that when the leaves of a plant are immersed in water and exposed to the rays of the sun, oxygen gas is disengaged. That the evolution of oxygen in this experiment is accompanied with a propor-

tional absorption of carbonic acid, is proved by employing water deprived of carbonic acid by boiling, in which case no oxygen is procured.

Such are the changes induced by plants when exposed to sun-shine; but in the dark an opposite effect ensues. Carbonic acid gas is not absorbed under these circumstances, nor is oxygen evolved; but, on the contrary, oxygen disappears and carbonic acid gas is disengaged. In the dark, therefore, vegetables deteriorate rather than purify the air, producing the same effect as the respiration of animals.

From several of the preceding facts, it is supposed that the oxygen emitted by plants while under the influence of light is derived from the carbonic acid which they absorb, and that the carbon of that gas is applied to the purposes of nutrition. Consistently with this view it has been observed that plants do not thrive when kept in an atmosphere of pure oxygen: and it was found by Dr Percival and Mr Henry, that the presence of a little carbonic acid is even favourable to their growth. Saussure, who examined this subject minutely, ascertained that plants grow better in an atmosphere which contains about one-twelfth of carbonic acid, than in common air, provided they are exposed to sunshine. But if that gas be present in a greater proportion, its influence is prejudicial; in an atmosphere consisting of one-half of its volume of carbonic acid, the plants perished in seven days, and they did not vegetate at all when that gas was in the proportion of two-thirds. In the shade, the presence of carbonic acid is always detrimental. He likewise observed that the presence of oxygen is necessary, in order that a plant should derive benefit from admixture with carbonic acid.

Saussure is of opinion that plants derive a large quantity of their carbon from the carbonic acid of the atmosphere, an opinion which receives great weight from the two following comparative experiments. On causing a plant to vegetate in pure water, supplied with common air and exposed to light, the carbon of the plant increased in quantity; but when supplied with common air, in a dark situation, it even lost a portion of the carbon which it had previously possessed.

Light is necessary to the colour of plants. The experiments of Sennebier and Mr Gough have shown that the green colour of the leaves is not developed, except when they are in a situation to absorb oxygen and give out carbonic acid.

Though the experiments of different philosophers agree as to the influence of vegetation on the air in sunshine and during the night, considerable uncertainty prevails both as to the phenomena occasioned by diffused daylight, and concerning the total effect produced by plants on the constitution of the atmosphere. Priestley found that air, vitiated by combustion or the respiration of animals, and left in contact for several days and nights with a sprig of mint, was gradually restored to its original purity; and hence he inferred that the oxygen gas consumed during these and various other processes, is restored to the mass of the atmosphere by the agency of growing vegetables.

This doctrine receives confirmation from the researches of Ingenhousz and Saussure, who were led to adopt the opinion that the quantity of oxygen gas evolved from plants by day, exceeds that of carbonic acid emitted during the night. The conclusions of Mr Ellis, on the contrary, are precisely the reverse. From an extensive series of experiments, contrived with much sagacity, Mr Ellis inferred that growing plants give out oxygen only in direct sunshine, while at all other times they absorb it; that when exposed to the ordinary vicissi-

tudes of sunshine and shade, light and darkness, they form more carbonic acid in the period of a day and night than they destroy; and, consequently, that the general effect of vegetation on the atmosphere is the same as that produced by animals. (Ellis's Researches and Farther Inquiries on Vegetation, &c.)

This question has been ably discussed by Sir H. Davy, in his Elements of Agricultural Chemistry. Sir H. Davy is of opinion that the experiments of Mr Ellis cannot be regarded as decisive, having been conducted under circumstances unfavourable to accuracy of result. He considers the original experiments of Priestley as unexceptionable, and adduces others made by himself in support of the same doctrine.

### On the Food of Plants.

The chief source from which plants derive the materials for their growth is the soil. However various the composition of the soil, it consists essentially of two parts, so far as its solid constituents are concerned. One is a certain quantity of earthy matters, such as siliceous earth, clay, lime, and sometimes magnesia; the other is formed from the remains of animal and vegetable substances, which, when mixed with the former, constitute common mould. A mixture of this kind, moistened by rain, affords the proper nourishment of plants. The water, percolating through the mould, dissolves the soluble salts with which it comes in contact, together with the gaseous, extractive, and other matters which are formed during the decomposition of the animal and vegetable remains. In this state it is readily absorbed by the roots, and conveyed as sap to the leaves, where it undergoes a process of assimilation.

But though this is the natural process by which plants obtain the greater part of their nourishment, and without which they do not arrive at perfect maturity, they may live, grow, and even increase in weight, when wholly deprived of nutrition from this source. Thus in the experiment of Saussure, already described, sprigs of peppermint were found to vegetate in distilled water; and it is well known that many plants grow when merely suspended in the air. In the hot-houses of the botanical garden of Edinburgh, for example, there are two plants, species of the fig-tree, the *ficus australis* and *ficus elastica*, the latter of which, as Dr Graham informs me, has been suspended for more than two, and the former for eight years, during which time they have continued to send out shoots and leaves.

Before scientific men had learned to appreciate the influence of atmospheric air on vegetation, the increase of carbonaceous matter, which occurs in some of these instances, was supposed to be derived from water, an opinion naturally suggested by the important offices performed by this fluid in the vegetable economy. Without water, plants speedily wither and die. It gives the soft parts that degree of succulence necessary for the due performance of their functions;—it affords two elements, oxygen and hydrogen, which, either as water, or under some other form, are contained in all vegetable products;—and, lastly, the roots absorb from the soil those substances only which are dissolved or suspended in water. So carefully, indeed, has nature provided against the chance of deficient moisture, that the leaves are endowed with a property both of absorbing aqueous vapour directly from the atmosphere, and of lowering their temperature during the night by radiation, so as to cause a deposition of dew upon

their surface, in consequence of which they frequently, during the driest seasons and in the warmest climates, continue to convey this fluid to the plant, when it can no longer be obtained in sufficient quantity from the soil. But necessary as is this fluid to vegetable life, it cannot yield to plants a principle which it does not possess. The carbonaceous matter which accumulates in plants, under the circumstances above mentioned, may, with every appearance of justice, be referred to the atmosphere; since we know that carbonic acid exists there, and that growing vegetables have the property of taking carbon from that gas.

When plants are incinerated, their ashes are found to contain saline and earthy matters, the elements of which, if not the compounds themselves, are supposed to be derived from the soil. Such at least is the view deducible from the researches of Saussure, and which might have been anticipated by reasoning on chemical principles. The experiments of M. Schrader, however, lead to a different conclusion. He sowed several kinds of grain, such as barley, wheat, rye, and oats, in pure flowers of sulphur, and supplied the shoots as they grew, with nothing but air, light, and distilled water. On incinerating the plants, thus treated, they yielded a greater quantity of saline and earthy matters than were originally present in the seeds.

These results, supposing them accurate, may be accounted for in two ways. It may be supposed, in the first place, that the foreign matters were introduced accidentally from extraneous sources, as by fine particles of dust floating in the atmosphere; or, secondly, it may be conceived, that they were derived from the sulphur, air, and water, with which the plants were supplied. If the latter opinion be adopted, we must infer either that the vital principle, which certainly controls chemical affinity in a surprising manner, and directs this power in the production of new compounds from elementary bodies, may likewise convert one element into another; or that some of the substances, supposed by chemists to be simple, such as oxygen and hydrogen, are compounds, not of two, but of a variety of different principles. As these conjectures are without foundation, and are utterly at variance with the facts and principles of the science, I do not hesitate in adopting the more probable opinion, that the experiments of M. Schrader were influenced by some source of error which escaped detection.



## ANIMAL CHEMISTRY.

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ALL distinct compounds, which are derived from the bodies of animals, are called *proximate animal principles*. They are distinguished from inorganic matter by the characters stated in the introduction to inorganic chemistry. The circumstances which serve to distinguish them from vegetable matter are, the presence of nitrogen, their strong tendency to putrefy, and the highly offensive products to which their spontaneous decomposition gives rise. It should be remembered however, that nitrogen is likewise a constituent of many vegetable substances; though few of these, the vegeto-animal principles excepted, (page 397) are prone to suffer the putrefactive fermentation. It is likewise remarkable that some compounds of animal origin, such as cholesterine and the oils, do not contain nitrogen as one of their elements, and are not disposed to putrefy.

The essential constituents of animal compounds are carbon, hydrogen, oxygen, and nitrogen, besides which some of them contain phosphorus, sulphur, iron, and earthy and saline matters in small quantity. Owing to the presence of sulphur and phosphorus, the process of putrefaction, which will be particularly described hereafter, is frequently attended with the disengagement of sulphuretted and phosphuretted hydrogen gases. When heated in close vessels, they yield water, carbonic oxide, carburetted hydrogen, probably free nitrogen and hydrogen, the carbonate and hydrocyanate of ammonia, and a peculiarly fetid thick oil. The carbonaceous matter left in the retort is less easily burned, and is more effectual as a decolorizing agent, than charcoal derived from vegetable matter.

The principle of the method of analyzing animal substances has already been mentioned. (Page 349.)

In describing the proximate animal principles, the number of which is far less considerable than the vegetable compounds, I shall adopt the arrangement suggested by Gay-Lussac and Thénard in their *Recherches Physico-Chimiques*, and followed by Thénard in his *System of Chemistry*. The animal compounds are accordingly arranged in three sections. The first contains substances which are neither acid nor oleaginous; the second comprehends the vegetable acids; and the third includes the animal fats. Several of the principles belonging to the first division, such as fibrin, albumen, gelatine, caseous matter, and urea, were shown by Gay-Lussac and Thénard to have several points of similarity in their composition. They all contain, for example, a large quantity of carbon, and their hydrogen is in such proportion as to convert all their oxygen into water, and their nitrogen into ammonia. No general laws have been established relative to the constitution of the compounds comprised in the other sections.

## SECTION I.

## SUBSTANCES WHICH ARE NEITHER ACID NOR OLEAGINOUS.

*Fibrin.*

Fibrin enters largely into the composition of the blood, and is the basis of the muscles; it may be regarded, therefore, as one of the most abundant of the animal principles. It is most conveniently procured by stirring recently drawn blood with a stick during its coagulation, and then washing the adhering fibres with water until they are perfectly white. It may also be obtained by removing the soluble parts from lean beef, cut into small slices, by digestion in several successive portions of water.

Fibrin is solid, white, insipid, and inodorous. When moist it is somewhat elastic, but on drying it becomes hard, brittle, and semi-transparent. In a moist warm situation it readily putrefies. It is insoluble in water at common temperatures, and is dissolved in very minute quantity by the continued action of boiling water. Alcohol, of density 0.81, converts it into a fatty adipocirous matter, which is soluble in alcohol and ether, but is precipitated by water.

The action of acids on fibrin has been particularly described by Berzelius\*. Digested in concentrated acetic acid fibrin swells and becomes a bulky tremulous jelly, which dissolves completely, with disengagement of a little nitrogen, in a considerable quantity of hot water.

By the action of nitric acid, of specific gravity 1.25, aided by heat, on fibrin, a yellow solution is formed, with disengagement of a large quantity of nearly pure nitrogen, in which Berzelius could not detect the least trace of the deutoxide of nitrogen. After digestion for twenty-four hours a pale yellow pulverulent substance is deposited, which Fourcroy and Vauquelin described as a new acid under the name of *yellow acid*. According to Berzelius, however, it is a compound of modified fibrin and nitric, together with some malic and nitrous acids. It likewise contains some fatty matter, which may be removed by alcohol. The origin of the nitrogen, which is disengaged in the beginning of the process, is somewhat obscure. From the total absence of the deutoxide of nitrogen, it is probable that, in the early stages, very little, if any, of the nitric acid is decomposed, and that the nitrogen gas is solely or chiefly derived from the fibrin.

Dilute muriatic acid hardens without dissolving fibrin, and the strong acid decomposes it. The action of sulphuric acid, according to M. Braconnot, is very peculiar. When fibrin is mixed with its own weight of concentrated sulphuric acid, a perfect solution ensues without change of colour, or disengagement of sulphurous acid. On diluting with water, boiling for nine hours, and separating the acid by means of chalk, the filtered solution was found to contain a peculiar white matter, to which M. Braconnot has applied the name of *leucine*. (An. de Ch. et de Ph. vol. xiii.) Digested in strong sulphuric acid a dark

\* Medico-Chirurgical Transactions, vol. iii. p. 201, et seq.

reddish-brown, nearly black solution, is formed, and the fibrin is carbonized and decomposed.

Fibrin is dissolved by pure potassa, and is thrown down when the solution is neutralized. The fibrin thus precipitated, however, is partially changed, since it is no longer soluble in acetic acid. It is soluble likewise in ammonia.

According to the analysis of Gay-Lussac and Thénard, 100 parts of fibrin are composed of carbon 53.36, hydrogen 7.021, oxygen 19.685, and nitrogen 19.934. From these numbers fibrin may be regarded as an atomic compound of carbon 18 atoms, hydrogen 14 atoms, oxygen 5 atoms, and nitrogen 3 atoms.

### *Albumen.*

Albumen enters largely into the composition both of animal fluids and solids. Dissolved in water it forms an essential constituent of the serum of the blood, the liquor of the serous cavities, and the fluid of dropsy; and in a solid state it is contained in several of the textures of the body, such as the cellular membrane, the skin, glands, and vessels. From this it appears that albumen exists under two forms, liquid and solid.

Liquid albumen is best procured from the white of eggs, which consists almost solely of this principle, united with water and free soda, and mixed with a small quantity of saline matter. In this state it is a thick glairy fluid, insipid, inodorous, and easily miscible with cold water, in a sufficient quantity of which it is completely dissolved. When exposed in thin layers to a current of air, it dries, and becomes a solid and transparent substance, which retains its solubility in water, and may be preserved for any length of time without change. Kept in its fluid condition it readily putrefies. From the free soda which they contain, albuminous liquids have always an alkaline reaction.

Liquid albumen is coagulated by heat, alcohol, and the stronger acids. Undiluted albumen is coagulated by a temperature of  $160^{\circ}$ , and when diluted with water at  $212^{\circ}$  F. Water which contains only 1-1000th of its weight of albumen is rendered opaque by boiling. (Bostock.) On this property is founded the method of clarifying by means of albuminous solutions; for the albumen being coagulated by heat, entangles in its substance all the foreign particles which are not actually dissolved, and carries them with it to the surface of the liquid. The character of being coagulated by hot water distinguishes albumen from all other animal fluids.

The acids differ in their action on albumen. The sulphuric, muriatic, nitric, and phosphoric acids coagulate it, and in each case, according to Thénard, some of the acid is retained by the albumen. Its solution is not precipitated at all by acetic acid. By maceration in dilute nitric acid for a month, it is converted, according to Mr Hatchett, into a substance soluble in hot water, and possessed of the leading properties of gelatine. Digested in strong sulphuric acid, the coagulum is dissolved, and a dark solution is formed similar to that produced by the same acid on fibrin; but if the heat be applied very cautiously, the liquid assumes a beautiful red colour. This property, which appears to be characteristic of albumen, was discovered some years ago by Dr Hope, who informs me that the experiment does not always succeed, the result being influenced by very slight causes.

Albumen is precipitated by several re-agents, especially by metallic

salts. This effect is produced by the muriate of tin, sub-acetate of lead, muriate of gold, and solution of tannin. Corrosive sublimate is a very delicate test of the presence of albumen, causing a milkiness when the albumen is diluted with 2000 parts of water. The nature of the precipitate has already been explained. (Page 296.) The ferrocyanate of potassa is equally delicate, provided a little acetic acid is previously added to neutralize the free soda.

When an albuminous liquid is exposed to the agency of galvanism, pure soda makes its appearance at the negative wire, and the albumen coagulates around that which is in connexion with the positive pole of the battery. Mr Brande\*, who first observed this phenomenon, ascribes it to the separation of free soda, upon which he supposes the solubility of albumen in water to depend; but M. Lassaigne† attributes it to the decomposition of muriate of soda, the acid of which coagulates the albumen. However this may be, galvanism is one of the most elegant and delicate tests of the presence of albumen in animal fluids which we possess.

Chemists are not agreed as to the cause of the coagulation of albumen. When it is coagulated by different chemical agents, such as tannin and metallic salts, the albumen is thrown down in consequence of forming an insoluble compound with the substance employed; and perhaps this is also the mode by which acids coagulate it. With respect to the agency of heat, alcohol, and probably of acids, a different view must be adopted. The explanation usually given is that proposed by Dr Thomson, who ascribes the solubility of albumen to the presence of free soda, and its coagulation to the removal of the alkali. To this hypothesis Dr Bostock objects, and with every appearance of justice, that albuminous liquids do not contain a sufficient quantity of free alkali for the purpose. (Medico-Chir. Trans. vol. ii. p. 175.) Were I to hazard an opinion on this subject, it would be the following:—that albumen combines directly with water at the moment of being secreted, at a time when its particles are in a state of minute division; but as its affinity for that liquid is very feeble, the compound is decomposed by slight causes, and for the same reason the albumen becomes quite insoluble, as soon as it is rendered solid by coagulation. Silica affords us an instance of a similar phenomenon. (Page 253.)

Albumen coagulates without appearing to undergo any change of composition, but it is quite insoluble in water, and is less liable to putrefy than in its liquid state. It is dissolved by alkalies with disengagement of ammonia, and is precipitated from its solution by acids. In the coagulated state it bears a very close resemblance to fibrin, and is with difficulty distinguished from it. Alcohol, ether, acids, and alkalies, according to Berzelius, act upon each in the same manner. He observes, however, that acetic acid and ammonia dissolve fibrin more easily than coagulated albumen. According to Thénard, they are readily distinguished by means of the deutoxide of hydrogen, from which fibrin causes evolution of oxygen, while albumen has no action upon it.

Albumen has been analyzed by Gay-Lussac and Thénard, and Dr Prout, with the following results:—

\* Philosophical Transactions for 1809.

† An. de Ch. et de Ph. vol. xx.

## Gay-Lussac and Thénard.

## Dr Prout.

Carbon,	52.883, 17 atoms.	50,	15 atoms.
Hydrogen,	7.540, 13 atoms.	7.78,	14 atoms.
Oxygen,	23.872, 6 atoms.	26.67,	6 atoms.
Nitrogen,	15.705, 2 atoms.	15.55,	2 atoms.
	<hr/> 100.000		<hr/> 100.00

## Gelatine.

Gelatine exists abundantly in many of the solid parts of the body, especially in the skin, cartilages, tendons, membranes and bones. According to Berzelius, it is not contained in any of the healthy animal fluids; and Dr Bostock, with respect to the blood, has demonstrated the accuracy of this statement. (Medico-Chir. Trans. vol. i. and ii.)

Gelatine is distinguished from all animal principles by its ready solubility in boiling water, and by the solution forming a bulky, semitransparent, tremulous jelly as it cools. Its tendency to gelatinize is such, that one part of gelatine, dissolved in 100 parts of water, becomes solid in cooling. This jelly is a hydrate of gelatine, and contains so much water, that it readily liquefies when warmed. On expelling the water by a gentle heat, a brittle mass is left, which retains its solubility in hot water, and may be preserved for any length of time without change. Jelly, on the contrary, soon becomes acid by keeping, and then putrefies.

The common gelatine of commerce is the well-known cement called *glue*, which is prepared by boiling cuttings of parchment, or the skins, ears, and hoofs of animals, and evaporating the solution. Isinglass, which is the purest variety of gelatine, is prepared from the sounds of fish of the genus *acipenser*, especially from the sturgeon. The animal jelly of the confectioners is made from the feet of calves, the tendinous and ligamentous parts of which yield a large quantity of gelatine.

Gelatine is insoluble in alcohol, but is dissolved readily by most of the diluted acids, which form an excellent solvent for it. Mixed with twice its weight of concentrated sulphuric acid, it dissolves without being charred; and on diluting the solution with water, boiling for several hours, separating the acid by means of chalk, and evaporating the filtered liquid, a peculiar saccharine principle is deposited in crystals. This substance has a sweet taste, somewhat like that of the sugar of grapes, is soluble in water, though less so than common sugar, and is insoluble in alcohol. When heated to redness, it yields ammonia as one of the products, a circumstance which shows that it contains nitrogen. Mixed with yeast, its solution does not undergo the vinous fermentation; and it combines directly with the nitric acid. It is hence apparent that, though possessed of a sweet taste, it differs entirely from sugar. This substance was discovered by M. Braconnot. (An. de Ch. et de Ph. vol. xiii.)

Gelatine is dissolved by the liquid alkalies, and the solution is not precipitated by acids.

Gelatine manifests little tendency to unite with metallic oxides. Corrosive sublimate and subacetate of lead do not occasion any



precipitate in a solution of gelatine, and the salts of tin and silver affect it very slightly. The best precipitate for it is tannin. By means of an infusion of gall-nuts, Dr Bostock detected the presence of gelatine when mixed with 5000 times its weight of water; and its quantity may even be estimated approximatively by this reagent. But since other animal substances, as for example albumen, are precipitated by tannin, it cannot be relied on as a test of gelatine. The best character for this substance is that of solubility in hot water, and of forming a jelly as it cools.

According to the analysis of gelatine by Gay-Lussac and Thénard, 100 parts of this substance consist of carbon, 47.881, hydrogen, 7.914, oxygen, 27.207, and nitrogen, 16.998. From these numbers it appears that its composition, as to the relative quantity of its elements, is identical with that of albumen as determined by Dr Prout.

### *Urea.*

Pure Urea is procured by evaporating fresh urine to the consistence of a syrup, and then gradually adding to it, when quite cold, pure concentrated nitric acid, till the whole becomes a dark-coloured crystallized mass, which is to be slightly washed with cold water, and then dried by pressure between folds of bibulous paper. To the nitrate of urea, thus procured, a pretty strong solution of the carbonate of potassa or soda is added, until the acid is neutralized, and the solution is afterwards concentrated by evaporation, and set aside, in order that the nitre may separate in crystals. The residual liquid, which is an impure solution of urea, is made up into a thin paste with animal charcoal, and is allowed to remain in that state for a few hours. The paste is then mixed with cold water, which takes up the urea, while the colouring matter is retained by the charcoal; and the colourless solution is evaporated to dryness at a low temperature. The residue is then boiled in pure alcohol, by which the urea is dissolved, and from which it is deposited in crystals on cooling.

Dr Prout, to whom we are indebted for the foregoing process for preparing pure urea, has given the following account of its properties. (*Medico-Chir. Trans.* vol. viii. p. 529.) Its crystals are transparent and colourless, of a slight pearly lustre, and have commonly the form of a four-sided prism. It leaves a sensation of coldness on the tongue like nitre. Its smell is faint and peculiar, but not urinous. Its specific gravity is about 1.35. It does not affect the colour of litmus or turmeric paper. In a moist atmosphere it deliquesces slightly; but otherwise undergoes no change on exposure to the air. Exposed to a strong heat, it melts, and is partly decomposed, and partly sublimes, apparently without change. The chief product of the decomposition, besides inflammable gas of a very fetid odour, benzoic acid and charcoal, is carbonate of ammonia.

Water at 60° dissolves more than its own weight of urea, and boiling water takes up an unlimited quantity of it. It requires for solution about five times its weight of alcohol, of density 0.816, at 60° F. and rather less than its own weight at a boiling temperature. The aqueous solution of pure urea may be exposed to the atmosphere for several months, or be heated to the boiling point, without change; but on the contrary, if the other constituents of the urine are present, it putrefies with rapidity, and is decomposed by a temperature of 212° F.,

being almost entirely resolved into carbonate of ammonia by continued ebullition.

The pure fixed alkalies and alkaline earths decompose urea, especially by the aid of heat, carbonate of ammonia being the chief product.

Though urea has not any distinct alkaline properties, it unites with the nitric and oxalic acids, forming sparingly soluble compounds, which crystallize in scales of a pearly lustre. This property affords an excellent test of the presence of urea. Both compounds have an acid reaction, and the nitrate consists of nitric acid 54 parts or one atom, and 60 parts or two atoms of urea.

The constituents of urea, according to the analysis of Dr Prout, are in the proportion of 6 parts or one atom of carbon, 2 or two atoms of hydrogen, 8 or one atom of oxygen, and 14 or one atom of nitrogen. Its atomic weight, therefore, is 30.

### *Sugar of Milk and Sugar of Diabetes.*

*Sugar of Milk.*—The saccharine principle of milk is obtained from whey by evaporating that liquid to the consistence of syrup, and allowing it to cool. It is afterwards purified by means of albumen and a second crystallization.

The sugar of milk has a sweet taste, though less so than the sugar of the cane, from which it differs essentially in several other respects. Thus it requires seven parts of cold and four of boiling water for solution, and is insoluble in alcohol. It is not susceptible of undergoing the vinous fermentation; and when digested with nitric acid it yields the saccholactic acid, a property first noticed by Scheele, and which distinguishes the saccharine principle of milk from every other species of sugar. Like starch, it is convertible into real sugar by being boiled in water acidulated with sulphuric acid.

The sugar of milk contains no nitrogen, and according to the analysis of Gay-Lussac and Thénard, is very analogous to common sugar in the proportion of its elements.

*Sugar of Diabetes.*—In the disease called *Diabetes*, the urine contains a peculiar saccharine matter, which, when properly purified, appears identical both in properties and composition to vegetable sugar, approaching nearer to the sugar of grapes than that from the sugar cane. Dr Prout found a minute quantity of nitrogen in it, but this gas, from its minute quantity, most probably originated in some animal matter derived from the urine.

This kind of sugar is obtained in an irregularly crystalline mass by evaporating diabetic urine to the consistence of syrup, and keeping it in a warm place for several days. It is purified by washing the mass with cold alcohol or at most gently heated, till that liquid comes off colourless, and then dissolving it in hot alcohol. By repeated crystallization it is thus rendered quite pure. (Prout.)

Two other principles yet remain to be considered, namely, the colouring principle of the blood, and caseous matter; but they will be more conveniently studied in subsequent sections.

## SECTION II.

## ANIMAL ACIDS.

In animal bodies several acids are found, such as the sulphuric, muriatic, phosphoric, acetic, &c., which belong equally to the mineral or vegetable kingdom, and which have consequently been described in other parts of the work. In this section are included those acids only which are believed to be peculiar to animal bodies.

*Uric, Purpuric, Rosacic, Formic and Lactic Acids, &c.*

*Uric or Lithic acid.*—This acid is a common constituent of urinary and gouty concretions, and is always present in healthy urine, combined with ammonia or some other alkali. The urine of birds of prey, such as the eagle, and of the *Boa Constrictor* and other serpents, consists almost solely of urate of ammonia, from which pure uric acid may be procured by a very simple process. For this purpose the solid urine of the *Boa Constrictor* is reduced to a fine powder, and digested in a solution of pure potassa, in which it is readily dissolved with disengagement of ammonia. The urate of potassa is then decomposed by adding the acetic, muriatic, or sulphuric acid in slight excess, when the uric acid is thrown down, and after being washed, is collected on a filter. On its first separation from the alkali it is in the form of a gelatinous hydrate, but in a short time this compound is decomposed spontaneously, and the uric acid subsides in small crystals. Pure uric acid is white, tasteless and inodorous. It is insoluble in alcohol, and is dissolved very sparingly by cold or hot water, requiring about 10,000 times its weight of that fluid at 60° F. for solution. (Prout.) It reddens litmus paper, and unites with alkalies, forming salts which are called *urates* or *lithates*. The uric acid does not effervesce with alkaline carbonates; but Dr Thomson affirms that when boiled for some time with the carbonate of soda, the whole of the carbonic acid is expelled. A current of carbonic acid, on the contrary, throws down the uric acid when dissolved by potassa. This acid undergoes no change by exposure to the air.

Of the acids none exert any peculiar action on the uric excepting the nitric acid. When a few drops of nitric acid, slightly diluted, are mixed on a watch glass with uric acid, and the liquid is evaporated to dryness, a beautiful purple colour comes into view, the tint of which is improved by the addition of water. This character affords an unequivocal test of the presence of uric acid. The nature of the change will be considered immediately.

Uric acid is decomposed by chlorine. On transmitting that gas through water in which uric acid is suspended, the latter disappears, and the liquid is found to contain the oxalic and malic acids, and muriate of ammonia.

Uric acid has been repeatedly analysed by Dr Prout, and its constituents, according to his latest analysis, (*Medico-Chir. Trans.* vol. ix.) are in the following proportions:—

Carbon	.	36	.	or	6 atoms.
Hydrogen	.	2	.	.	2
Oxygen	.	24	.	.	3
Nitrogen	.	28	.	.	2

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90

The crystallized acid, as analyzed by Prout, is supposed by most chemists to be anhydrous; but Dr Thomson maintains that on exposing 90 parts of it to a temperature of 400° F. it loses 18 parts, or the equivalent of two atoms of water, and that the residue is the real anhydrous uric acid, composed of carbon 6 atoms, oxygen 1 atom, and nitrogen 2 atoms. On this view the atomic weight of uric acid is 72, a number which Dr Thomson has deduced from his analysis of the urate of soda.

The salts of uric acid have been described by Dr Henry. (Manchester Memoirs, vol. ii. N.S.) The only ones of importance are the urates of ammonia, potassa, and soda. The urate of ammonia is soluble to a considerable extent in boiling, but more sparingly in cold water. The urates of soda and potassa, if neutral, are of very sparing solubility; but an excess of either alkali takes up a large quantity of the acid. The former was found by Dr Wollaston to be the chief constituent of gouty concretions.

*Pyro-uric acid*.—When uric acid is exposed to heat in a retort, the carbonate and hydrocyanate of ammonia are formed, together with a peculiar volatile acid, called *pyro-uric acid*, which was formerly described by Dr Henry, and has recently been particularly studied by MM. Chevalier and Lassaigne. (Ann. of Phil. vol. xvi.)

This acid sublimes without change, and condenses on cool surfaces in the form of white acicular crystals. It is soluble in boiling alcohol, and requires forty times its weight of water for solution. It is not decomposed by digestion in nitric acid, a character by which it is distinguished from uric acid.

*Purpuric acid*.—This compound was first recognised as a distinct acid by Dr Prout, and was described by him in the Philosophical Transactions for 1818. Though colourless itself, it has a remarkable tendency to form red or purple coloured salts with alkaline bases, a character by which it is distinguished from all other substances, and to which it owes the name of *purpuric acid*, suggested by Dr Wollaston. Thus the purple residue above mentioned, as indicative of the presence of uric acid, is the purpurate of ammonia, which is always generated when the uric is decomposed by the nitric acid.

This compound is prepared by digesting pure uric acid, extracted from the urine of the *boa constrictor*, in dilute nitric acid, when the former is dissolved with effervescence. The solution is then neutralized by ammonia, and concentrated by evaporation, during the course of which purple coloured crystals of the purpurate of ammonia are deposited. The purpurate of ammonia is then decomposed by digestion with pure potassa, and the liquid is gradually poured into dilute sulphuric acid. The purpuric acid is thus disengaged, and being insoluble in water, subsides to the bottom in the form of a white or yellowish-white powder, according to its degree of purity. This process, I may remark, is one of some delicacy;—I have repeatedly followed the steps recommended by Dr Prout, but have been as frequently disappointed in the attempt to procure the acid in an insulated state.

Considerable uncertainty prevails as to the nature of purpuric acid.

Vauquelin, for example, denies that its salts have a purple colour, but attributes that tint to the presence of some impurity. M. Lassaigue is likewise inclined to the same opinion. (An. de Ch. et de Ph. vol. xxii. p. 334.) The composition of the acid is a point equally unsettled; for Dr Prout has expressed a doubt of the accuracy of the analysis which he formerly published.

The name of *erythric acid* (from *ερυθραίνειν*, to *red*den) was applied by Brugnatelli to a substance which he procured by the action of the nitric on uric acid. It obviously contains purpuric acid, and Dr Prout thinks it probable that it is a super-salt, consisting of purpuric and nitric acids, and ammonia.

*Rosacic acid*.—This name was applied by Proust to a peculiar acid supposed to exist in the red matter, commonly called by medical practitioners the *lateritious sediment*, which is deposited from the urine in some stages of fever. From the experiments of Vogel it appears to be the uric acid, either combined with an alkali, or modified by the presence of animal matter. Dr Prout is of opinion that it contains some purpurate of ammonia; and, as he has detected the presence of nitric acid in the urine from which such sediments were deposited, he thinks it probable that the purpurate may be generated by the reaction of the uric and nitric acids on each other in the urinary passages.

*Formic acid*.—The acid extracted from ants was for some time suspected, chiefly on the authority of Fourcroy and Vauquelin, to be a mixture of the acetic and malic acids; but the experiments of Suersen, Gehlen, Berzelius, and Döbereiner appear to leave no doubt of its being a distinct compound. In volatility and odour it does, indeed, resemble the acetic acid; but in composition it is entirely different. According to the analysis of the formate of lead by Berzelius, the atomic weight of formic acid is inferred to be 37; and it is composed of carbon 12 parts or two atoms, hydrogen 1 or one atom, and 24 parts or three atoms of oxygen. It hence differs from oxalic acid only in containing one atom of hydrogen. According to Döbereiner it is resolved into carbonic oxide and water by the action of strong sulphuric acid. The same ingenious chemist has succeeded in preparing formic acid artificially, by applying a gentle heat to a mixture of tartaric acid, water, and the protoxide of manganese. The tartaric acid is converted into water, carbonic acid, and formic acid. (An. of Phy. vol. iv. N. S.)

*Lactic acid*.—The existence of this acid, though described by Berzelius, and found by him in sour milk and in many animal fluids, was never demonstrated in a satisfactory manner. Berzelius himself now admits it to be the acetic acid disguised by animal matter, an opinion which is confirmed by Tiedemann and Gmelin in their experimental Essay on Digestion. (Die Verdauung nach Versuche. Heidelberg, 1826.)

The *Amniotic* is a weak acid which was discovered by Buniva and Vauquelin in the liquor of the Amnios of the cow, from which it is deposited by gentle evaporation in the form of white acicular crystals. It is very sparingly soluble in water, but yields with the alkalies soluble compounds which are decomposed by most of the acids.

Several other animal acids, such as the stearic, oleic, margaric, and others, should also be mentioned here; but as they are closely allied to the fatty principles from which they are derived, they will be more conveniently described in the following section.



## SECTION III.

## OLEAGINOUS SUBSTANCES.

*Animal Oils and Fats.*

The fatty principles derived from the bodies of animals are very analogous in composition and properties to the vegetable fixed oils; and in Britain, where the latter are comparatively expensive, the former are employed, both for the purposes of giving light, and for the manufacture of soap. Their ultimate elements are carbon, hydrogen, and oxygen; and most of them, like the fixed oils, consist of stearine and elaine.

From a curious experiment of Bérard it appears that a substance very analogous to fat may be made artificially. On mixing together one measure of carbonic acid, ten measures of carburetted hydrogen, and twenty of hydrogen, and transmitting the mixture through a red hot tube, several white crystals were obtained, which were insoluble in water, soluble in alcohol, and fusible by heat into an oily fluid. (An. of Ph. vol. xii. p. 41.) Döbereiner prepared an analogous substance from a mixture of coal gas and aqueous vapour.

*Train oil.*—Train oil is obtained by means of heat from the blubber of the whale, and is employed extensively in making oil gas and for burning in common lamps. It is generally of a reddish or yellow colour, emits a strong unpleasant odour, and has a considerable degree of viscosity, properties which render it unfit for being burned in argand lamps, and which are owing partly to the heat employed in its extraction, and partly to the presence of impurities. By purification, indeed, it may be rendered more limpid, and its odour less offensive; but it is always inferior to spermaceti oil.

*Spermaceti oil* is obtained from an oily matter lodged in a bony cavity in the head of the *Physeter macrocephalus* or spermaceti whale. On subjecting this substance to pressure in bags, a quantity of pure limpid oil is expressed; and the residue, after being melted, strained, and washed with a weak solution of potassa, is sold under the name of *spermaceti*.

*Animal oil of Dippel.*—This name is applied to a limpid volatile oil, which is entirely different from the oils above mentioned, and is a product of the destructive distillation of animal matter, especially of albuminous and gelatinous substances. When purified by distillation it is clear and transparent. It was formerly much used in medicine, but is now no longer employed.

*Hogslard and suet.*—The most common kinds of fat are hogslard and suet, which differ from each other chiefly in the degree of consistency. The latter, when separated by fusion from the membrane in which it occurs, is called tallow, which is extensively employed in the manufacture of soap and candles. Both these varieties of fat, as well as train and spermaceti oil, consist almost entirely of stearine and elaine, and when converted into soap, undergo the same change as the fixed oils, yielding margaric and oleic acids, and the mild principle of oils called *glycerine*.

The method of preparing stearine and elaine from the vegetable oils has already been detailed; (page 374) and the same process, which

originated with M. Braconnot, is also applicable to hogslard. The mode by which M. Chevreul obtains these principles is by treating hogslard in successive portions of hot alcohol. The spirit in cooling deposits the stearine in the form of white crystalline needles, which are brittle, and have the aspect of wax, fuse readily when heated, and are insoluble in water. The alcoholic solution, when evaporated, leaves an oily fluid which is elaine. They may be then rendered quite pure by re-solution in boiling alcohol.

For the method of obtaining margaric and oleic acids in a state of perfect purity, I refer to the account of M. Chevreul in his treatise, *Sur les Corps Gras*. The principle of the process is the following:—a portion of hogslard is converted into soap by means of pure potassa, and the soap so formed, consisting of the margarate and oleate of that alkali, is separated as much as possible from adhering moisture by bibulous paper, and then treated by cold alcohol of specific gravity 0.821, in which the oleate is soluble, and the margarate insoluble. The two salts, being thus separated, are decomposed by means of an acid.

Margaric acid, so named from its pearly lustre, (from *μαργαρίτης* a pearl) is insoluble in water, dissolves freely in alcohol, especially by the aid of heat, and has an acid reaction. At 140° Fahr. it fuses, and shoots into brilliant white acicular crystals on cooling. Its salts, those of the alkalies excepted, are of very sparing solubility in water.

Oleic acid, at the mean temperature, is a colourless oily fluid, which congeals when it is cooled to near zero of Fahr. It has a slightly rancid odour and taste, and reddens litmus paper. Its specific gravity is 0.898. It is insoluble in water, but is dissolved in every proportion by alcohol. Of the neutral oleates hitherto examined, that of soda and potassa are alone soluble in water.

*Stearic acid*.—This acid is generated, together with the two former acids, during the conversion of suet into soap. In its properties it is closely allied to the margaric acid.

*Sebacic acid*.—M. Thénard has applied this name to an acid which is obtained by the distillation of hogslard or suet, and is found in the recipient mixed with acetic acid and fat, partially decomposed. It is separated from the latter by means of boiling water, and from the former by the acetate of lead. The sebate of lead, which subsides, is subsequently decomposed by sulphuric acid.

The sebacic acid reddens litmus paper, dissolves freely in alcohol, and is more soluble in hot than in cold water. It melts like fat when heated, and crystallizes in small white needles in cooling. It is not applied to any use.

*Butyric acid*.—Butter differs from the common animal fats in containing a peculiar oleaginous matter, which is quite fluid at 70° F., and to which M. Chevreul has applied the name of *butyric acid*. When converted into soap, it yields, in addition to the usual products, three volatile odoriferous compounds, namely, the *butyric*, *caproic* and *capric* acids.

*Phocénine* is a peculiar fatty substance contained in the oil of the porpoise (*Delphinium phocæna*) mixed with elaine. When converted into soap, it yields a volatile odoriferous acid, called the *phocénic acid*. (Chevreul.)

*Hircine* is contained in the fat of the goat and sheep, and yields the *hircine acid* when converted into soap. (Chevreul.)

*Spermaceti*.—This inflammable substance, which is prepared from the spermaceti whale, as above mentioned, commonly occurs in crys-

talline plates of a white colour and silvery lustre. It is brittle, and feels soft and slightly unctuous to the touch. It has no taste, and scarcely any odour. It is insoluble in water, but dissolves in about thirteen times its weight of boiling alcohol, from which the greater part is deposited on cooling in the form of brilliant scales. It is still more soluble in ether. It is exceedingly fusible, liquefying at a temperature which is distinctly below  $212^{\circ}$  F. Digested with pure potassa it is converted into soap.

The spermaceti of commerce always contains some fluid oil, from which it may be purified by solution in boiling alcohol. To the white crystalline scales deposited from the spirit as it cools, and which is spermaceti in a state of perfect purity, M. Chevreul has given the name of *cetine*.

*Adipocire*.—When a piece of fresh muscle is exposed for some time to the action of water, or is kept in moist earth, the fibrin entirely disappears, and a fatty matter called *adipocire* remains, which has some resemblance to spermaceti. The fibrin was formerly thought to be really converted into adipocire; but Gay-Lussac\* and Chevreul maintain that this substance proceeds entirely from the fat originally present in the muscle, and that the fibrin is merely destroyed by putrefaction. Dr Thomson maintains, however, that the conversion of fibrin into fat does occur in some instances, and has related a remarkable case in proof of his opinion. (Ann. of Phil. vol. xii. p. 41.) According to M. Chevreul, the adipocire is not a pure fatty principle, but a species of soap, chiefly consisting of margaric acid in combination with ammonia generated during the decomposition of the fibrin.

*Cholesterine*†.—This name is applied by M. Chevreul to the crystalline matter which constitutes the basis of most of the biliary concretions formed in the human subject. Fourcroy, regarding it as identical with spermaceti and the fatty matter just described, comprehended all these substances under the general appellation of adipocire; but M. Chevreul has shown that it is a distinct independent principle, wholly different from spermaceti.

Cholesterine is a white brittle solid of a crystalline lamellated structure and brilliant lustre, very much resembling spermaceti; but it is distinguished from that substance by requiring a temperature of  $278^{\circ}$  F. for fusion, and by not being convertible into soap when digested in a solution of potassa. It is free from taste and odour, and is insoluble in water. It dissolves freely in boiling alcohol, from which it is deposited on cooling in white pearly scales. When digested in an equal weight of nitric acid it yields a peculiar acid, called *cholesteric acid*, which was described by MM. Pelletier and Caventou in the third volume of the *Journal de Pharmacie*.

According to the analysis of M. Chevreul, cholesterine is composed of carbon 85.095, hydrogen 11.880, and oxygen 3.025.

Cholesterine has lately been detected in the bile of man, and of several of the lower animals, such as the ox, dog, pig and bear. This interesting discovery was made about the same time by Chevreul in Paris, and by Tiedemann and Gmelin in Heidelberg. M. Lassaigne has likewise found it in the biliary calculus of a pig. (An. de Ch. et de Ph. vol. xxxi.)

\* An. de Ch. et de Ph. vol. iv.

† From *χολη bile* and *στερεος solid*.

The best method of preparing pure cholesterine is to treat human biliary concretions, reduced to powder, with boiling alcohol, and to filter the hot solution as rapidly as possible. As the liquid cools, the greater part of the cholesterine subsides. In this way it is freed from the colouring matter with which it is commonly associated in the gall-stone.

*Ambergris*.—This substance is found floating on the surface of the sea near the coast of India, Africa, and Brazil, and is supposed to be a concretion formed in the stomach of the spermaceti whale. It has commonly been regarded as a resinous principle; but its chief constituent is a substance very analogous to cholesterine, and to which Pelletier and Caventou have given the name of *ambreine*. By digestion in nitric acid ambreine is converted into a peculiar acid, the *ambreic acid*. (An. of Phil. vol. xvi.)

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## ON THE MORE COMPLEX ANIMAL SUBSTANCES AND SOME FUNCTIONS OF ANIMAL BODIES.

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### SECTION I.

#### ON THE BLOOD.—RESPIRATION AND ANIMAL HEAT.

The blood, while circulating in the vessels of living animals, is fluid, and of a florid red colour in the arteries, and of a dark purple colour in the veins. Its taste is slightly saline, its odour peculiar, and to the touch it seems somewhat unctuous. Its specific gravity is variable, but most commonly is near 1.05, and in man its temperature is about 98° or 100° Fahr. When recently drawn, it appears to the naked eye as a uniform homogeneous fluid; but if examined with a microscope of sufficient power, numerous red particles of a globular form are seen floating in a colourless fluid. The compound nature of the blood is rendered still more apparent by the process of coagulation, during which it separates spontaneously into two distinct portions, a yellowish liquid called the *serum* of the blood, and a red solid, known by the name of the *clot*, *cruor*, or *crassamentum*. The proportion of these parts is variable, the latter being more abundant in healthy vigorous animals, than in those which have been debilitated by depletion, low living, or disease.

The serum is somewhat unctuous to the touch, of a saline taste, and of slightly alkaline reaction, owing to the presence of a little free soda. Its average specific gravity is about 1.029. Like other albuminous liquids, it is coagulated by heat, acids, alcohol, and all other substances which coagulate albumen. On subjecting the coagulum prepared by heat to gentle pressure, a small quantity of a colourless limpid fluid, called the *serosity*, oozes out, which contains, according to Dr Bostock, about 1-50th of its weight of animal matter, together with a little muriate of soda. Of this animal matter a portion is albumen, which may easily be coagulated by means of galvanism; but a small quantity of

some other principle is present, which differs both from albumen and gelatine. (Med. Chir. Trans. vol. ii. p. 166.)

From the analysis of the late Dr Marcet, 1000 parts of the serum of human blood are composed of water 900 parts, albumen 86.8, muriate of potassa and soda 6.6, muco-extractive matter 4, carbonate of soda 1.65, sulphate of potassa 0.35, and of earthy phosphates 0.60. This result agrees very nearly with that obtained by Berzelius, who states that the *extractive matter* of Marcet is lactate (acetate) of soda united with animal matter. (Med. Chir. Trans. vol. iii. p. 231.)

The crassamentum or clot of the blood consists of two parts, the fibrin and colouring principle. The latter resides in distinct particles, which, according to Prevost and Dumas, are elliptical in birds and cold-blooded animals, and assume the globular form in the mammiferous animals. These globules are insoluble in serum; but their colour is dissolved by pure water, acids, alkalies, and alcohol. Much uncertainty prevails among chemists relative to the cause of the colour of the red globules. As soon as the blood was known to contain iron, the peroxide of which has a red tint, the colour of the red globules was ascribed to the presence of that metal, and some chemists supposed it to be in the form of the sub-phosphate of iron. This opinion was adopted by Fourcroy and Vauquelin, who even affirmed that the phosphate of iron may be dissolved in serum by means of an alkali, and that the colour of the solution is exactly similar to that of the blood.

This subject was investigated in 1806 by Berzelius, who showed that the sub-phosphate of iron cannot be dissolved in serum, in the way supposed by Fourcroy and Vauquelin, except in very minute quantity: and that this salt, even when rendered soluble by phosphoric acid, communicates a tint quite different from that of the red globules. On comparing together the composition of the three principal ingredients of the blood, viz. fibrin, albumen, and colouring matter, he found that the ashes of the last always yielded oxide of iron in the proportion of 1-200th of the original mass, while the oxide was entirely wanting in the two former. From this it was a probable inference that iron is somehow or other concerned in the production of the red colour; but the experiments of Berzelius did not make known the state in which that metal exists in the blood. He could not detect its presence by any of the liquid tests. (Med. Chir. Trans. vol. iii. p. 213.)

In a series of experiments published in 1812, (Philos. Trans.) Mr Brande obtained results quite contrary to those of Berzelius. He detected iron in the ashes of the serum and fibrin as well as in those of the red globules; and in each it was present in such minute quantity, that no effect as a colouring agent could be expected from it. Mr Brande supposed that the tint of the red globules is produced by a peculiar animal colouring principle, capable, like other substances of a similar nature, of combining with metallic oxides. He succeeded in obtaining a compound of the colouring matter of the blood with the oxide of tin; but its best precipitants are the nitrate of mercury and corrosive sublimate. Woollen cloths impregnated with either of these compounds, on their being dipped into an aqueous solution of the colouring matter, acquired a permanent red dye, unchangeable by washing with soap.

The conclusions of Brande, relative to the presence of iron in the albumen and fibrin of the blood, received additional support from the researches of Vauquelin; (An. de Ch. et de Ph. vol. i.) but the question has been finally decided by Dr Engelhart, a young German che-



mist of great promise, who gained the prize offered in the year 1825 by the Medical Faculty of Göttingen for the best Essay on the nature of the colouring matter of the blood. (Edinb. Med. and Surg. Journal for January, 1827.) He demonstrated that the fibrin and albumen of the blood, when carefully separated from colouring particles, do not contain a trace of iron; and, on the contrary, he procured iron from the red globules by incineration. But he has likewise succeeded in proving the existence of iron in the colouring matter of the blood by the liquid tests; for on transmitting a current of chlorine gas through a solution of the red globules, the colour entirely disappeared, white flocks were thrown down, and a transparent solution remained, in which the peroxide of iron was discovered by all the usual re-agents. The results obtained by Dr Engelhart relative to the quantity of the iron, correspond with those of Berzelius. These facts have been since confirmed by M. Rose, who has accounted in a satisfactory manner for the failure of former chemists in detecting iron in the blood while in a fluid state. He finds that the oxide of iron cannot be precipitated by the alkalies, hydrosulphuret of ammonia, or infusion of galls, if it is dissolved in a solution which contains albumen or other soluble organic principles.

From the presence of iron in the red globules, and its total absence in the other principles of the blood, it is probable that this metal, though its quantity does not exceed one-half per cent., is essential to the production of the red colour. The experiments of Dr Engelhart, however, have not determined the manner in which it acts, nor in what state it exists in the blood, though it is most probably in the form of an oxide. It is a singular coincidence that the sulpho-cyanic acid, which forms with the peroxide of iron a colour exactly like that of venous blood, has been detected in the saliva. The existence of this acid in the blood itself is, therefore, a circumstance by no means improbable.

Dr Engelhart is likewise the first chemist who has procured the colouring matter of the blood in a state of perfect purity. The method formerly recommended is that of Berzelius, whose process consists in allowing the clot cut into thin slices to drain as much as possible on bibulous paper, triturating it with water, and then evaporating the solution at a temperature not exceeding 122° F. As thus prepared, the colouring matter retains all its properties, but is mixed with a little serum. The method of Dr Engelhart is founded on the fact, that serum, when much diluted, does not coagulate by heat, while the red particles are coagulated, and fall down in the form of brown flocks. Serum diluted with ten parts of water does not coagulate at 167° F.; but the colouring matter, dissolved in fifty parts of water, begins to coagulate at 149° F.

The colouring particles, when prepared in this way, are no longer of a bright red colour, and their nature is somewhat modified, in consequence of which they are insoluble in water. When half dried, they form a brownish-red, granular, friable mass; and when completely dried at a temperature between 167° and 190°, the mass is tough, hard, brilliant, black with reflected, and garnet-red with transmitted light. Except in their insolubility, they have all the properties of the red particles obtained by the method of Berzelius. The caustic alkalies with the aid of heat dissolve them entirely, and the solution acquires a dark blood-red colour.

The fibrin of the blood may easily be obtained in a pure state by

washing the clot in cold water until the colouring matter is entirely removed. While circulating in the animal body it is either in a fluid state, or suspended in the serum in the form of minute colourless globules; but when removed from the vessels and set at rest, it becomes solid in the course of a few minutes, giving rise to what is called the *coagulation* of the blood. The time required for coagulation is influenced by temperature, being promoted by heat, and retarded by cold. Dr Scudamore finds that blood which begins to coagulate in four minutes and a half in an atmosphere of 53° F. undergoes the same change in two minutes and a half at 98°; and that which coagulates in four minutes at 98° F. will become solid in one minute at 120°. On the contrary, blood which coagulates firmly in five minutes at 60° F. will remain quite fluid for twenty minutes at the temperature of 40° F., and requires upwards of an hour for complete coagulation. (Scudamore on the Blood.)

The process of coagulation is influenced by exposure to the air. If the atmospheric air be excluded, as by filling a bottle completely with recently drawn blood, and closing the orifice with a good stopper, coagulation is retarded. It is singular, however, that if blood be confined within the exhausted receiver of an air-pump, the coagulation is accelerated. (Scudamore.)

Recently drawn blood, owing doubtless to its temperature, is known to give off a portion of aqueous vapour, which has a peculiar odour, indicative of the presence of some peculiar principle, but in which nothing but water can be detected. Physiologists are not agreed upon the question whether the act of coagulation is or is not accompanied with the disengagement of gaseous matter. In the experiments of Vogel, Brande, and Scudamore, blood coagulating in the vacuum of an air-pump was found to emit carbonic acid, and Dr Scudamore even inferred that the evolution of this gas constitutes an essential part of the process. Other experimentalists, however, have obtained a different result. Dr John Davy and Dr Duncan, jun. failed in their attempts to procure carbonic acid from blood during coagulation; and Dr Christison, in an experiment performed two years ago in my laboratory, and at which I was present, was not more successful. These facts appear conclusive against the opinion of Dr Scudamore, and they receive additional weight from the consideration, that the appearance of carbonic acid in the experiments above mentioned, might easily have been occasioned by casual exposure to the atmosphere previous to the blood being placed under the receiver.

Coagulation is influenced by the rapidity with which the blood is removed from the body. Dr Scudamore observed, that blood slowly drawn from a vein coagulates more rapidly than when taken in a full stream.

Experiments are still wanting to show the influence of different gases on coagulation. Oxygen gas accelerates coagulation, and carbonic acid retards, but cannot prevent it.

Caloric is evolved during the coagulation of the blood. The late Dr Gordon estimated the rise of the thermometer at six degrees; and Dr Davy, on the other hand, regards the increase of temperature from this cause as very slight. Dr Scudamore finds that the rate at which blood cools is distinctly slower than it would be were no caloric disengaged, and he observed the thermometer to rise one degree at the commencement of coagulation.

Some substances prevent the coagulation of the blood. This effect

is produced by a saturated solution of muriate of soda, muriate of ammonia or nitre, and a solution of potassa. The coagulation, on the contrary, is promoted by alum and the sulphates of zinc and copper. The blood of persons who have died a sudden violent death, by some kinds of poison, or from mental emotion, is usually found in a fluid state. Lightning is said to have a similar effect; but Dr Scudamore declares this to be an error. Blood, through which electric discharges were transmitted, coagulated as quickly as that which was not electrified; and in animals killed by the discharge of a powerful galvanic battery, the blood in the veins was always found in a solid state.

The cause of the coagulation of the blood has been the subject of much speculation to physiologists. The tendency of this fluid to preserve the liquid form while contained in a living animal, cannot be ascribed to the motion to which it is continually subject within the vessels. It is a familiar fact, that blood, though continually stirred out of the body, is not prevented from coagulating; and it has been noticed, that the coagulation of blood, which is set at rest within its proper vessels by the application of ligatures, or which has been accidentally extravasated within the body, is materially retarded. It has, indeed, been hitherto found impossible to account in a satisfactory manner for the blood retaining its fluidity from the influence of motion, temperature, or the operation of any physical or chemical laws, and, consequently, it is generally ascribed to the agency of the vital principle. The blood is supposed either to be endowed with a principle of vitality, or to receive from the living parts with which it is in contact a certain vital impression, which, together with constant motion, counteracts its tendency to coagulate.

The clot of blood drawn from an individual in a state of health is red throughout its whole substance, because the fibrin coagulates before the red globules have had time to subside. In inflammatory diseases, on the contrary, the blood undergoes a peculiar change, in consequence of which the red globules sink to the bottom before the fibrin has become solid, and thus leave the upper surface of the latter of its natural pale colour. This appearance is familiarly known by the name of *buffy coat*. Its formation must obviously depend either on the coagulation being unusually slow, so that the red globules have full leisure to subside; or on the coagulation taking place in the ordinary period, while the red globules subside with unusual rapidity. The nature of the change which gives rise to the buffy coat is altogether unknown.

### *Respiration.*

When venous blood is brought into contact with atmospheric air, its surface passes from a dark purple to a florid red colour, oxygen disappears, and carbonic acid gas is emitted. These changes take place more speedily when air is agitated with blood; they are still more rapid when pure oxygen is substituted for atmospheric air; and they do not occur at all when oxygen is entirely excluded. It is hence inferred that the process of *arterialization*, as it is called, or the conversion of venous into arterial blood, depends entirely on the presence of oxygen. It is also presumed that the alternating shades of colour are caused by the red particles undergoing certain chemical changes, the nature of which, however, is at present quite inexplicable.

The same changes that occur out of the body are continually taking

place within it. During respiration, venous blood is exposed in the lungs to the agency of the air and is arterialized, oxygen disappears, and carbonic acid is evolved; and it is remarkable that these phenomena ensue not only during life, but even after death, provided the respiratory process be preserved artificially. Since, therefore, the essential phenomena of arterialization, according to the best data we possess, are the same in a living and in a dead animal, and whether the blood is or is not contained in the body, it seems quite legitimate to infer, that this process is not necessarily dependent on the vital principle, but is solely determined by the laws of chemical action.

In studying the subject of respiration the first object is to determine the precise change produced in the constitution of the air which is inhaled. Dr Black was the first to notice that the air exhaled from the lungs contains a considerable quantity of carbonic acid, which may be detected by transmission through lime water. Priestley, some years after, observed that air is rendered unfit for supporting flame or animal life by the process of respiration, from which it was probable that oxygen is consumed; and Lavoisier subsequently established the fact, that during respiration oxygen gas disappears, and carbonic acid is disengaged. The chief experimentalists who have since cultivated this department of chemical physiology are Priestley, Scheele, Lavoisier, Seguin, Crawford, Goodwin, Davy, Ellis, Allen and Pepys, Edwards and Despretz. Of these, the results obtained by Messrs Allen and Pepys\*, and Dr Edwards†, are the most conclusive and satisfactory, their researches being conducted with great care, and aided by all the resources of modern chemistry.

One of the chief objects of Messrs Allen and Pepys, in their experiments, was to ascertain if any uniform relation exists between the oxygen consumed and the carbonic acid evolved. They found in general that the quantity of the former exceeds that of the latter; but as the difference was very trifling they inferred that the carbonic acid of the expired air is exactly equal to the oxygen which disappears. The experiments of Dr Edwards were attended with a remarkable result, which accounts very happily for some of the discordant statements of preceding experimenters. He found the ratio between the gases to vary with the animal. In some animals it might be regarded as nearly equal; while in others, the loss of oxygen considerably exceeded the gain of carbonic acid, so that the respired air suffered a material diminution in volume. With respect to the human subject, the statement of Allen and Pepys seems very near the truth.

The quantity of oxygen withdrawn from the atmosphere, and of carbonic acid disengaged, is variable in different individuals, and in the same individual at different times. It is estimated by Allen and Pepys, that in every minute during the calm respiration of a healthy man of ordinary stature, 26.6 cubic inches of carbonic acid of the temperature of 50° F. are emitted, and an equal volume of oxygen withdrawn from the atmosphere. From these data it has been calculated that, in an interval of twenty-four hours, not less than eleven ounces of carbon are given off from the lungs alone,—an estimate which must surely be inaccurate, the quantity being so great as sometimes to exceed the weight of carbon contained in the food. From the observa-

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\* Philosophical Transactions for 1808.

† De l'Influence des Agens Physiques sur la Vie, 1824.



tions of Dr Prout, it appears that the quantity of carbonic acid emitted from the lungs is variable at particular periods of the day, and in particular states of the system. It is more abundant during the day than the night; about day-break it begins to increase, continues to do so till about noon, and then decreases until sunset. During the night it seems to remain uniformly at a minimum; and the maximum quantity given off at noon, exceeds the minimum by about one-fifth of the whole. The quantity of carbonic acid is diminished by any debilitating causes, such as low diet, depressing passions, and the like. (An. of Phil. vol. xiii. p. 269.) The experiments of Dr Fyfe, published in his Inaugural Dissertation, are confirmatory of those above mentioned.

Messrs Allen and Pepys have shown that the atmospheric air, when drawn into the lungs, returns charged in the succeeding expiration with from 8 to 8.6 per cent. of carbonic acid gas. They found also, that when an animal is confined in the same quantity of air, death ensues before all the oxygen is consumed; that when the same portion of air is repeatedly respired until it can no longer support life, it then contains only 10 per cent. of carbonic acid.

Although in respiration the arterialization of the blood by means of free oxygen is the essential change, without the due performance of which the life of warm blooded animals cannot be preserved beyond a few minutes, and which is likewise necessary to the lowest of the insect tribe, it is important to determine whether the nitrogen of the atmosphere has any influence in the function. The results of different inquirers differ considerably. In the experiments of Priestley, Davy, Humboldt, Henderson and Pfaff, there appeared to be absorption of nitrogen, a less quantity of that gas being exhaled than was inspired. Nysten, Berthollet, and Despretz, on the contrary, remarked an increase in the bulk of the nitrogen; and from the researches of Seguin and Lavoisier, Vauquelin, Ellis, Dalton and Spallanzani, it was inferred that there is neither absorption nor exhalation of nitrogen, the quantity of that gas undergoing no change during its passage through the air cells of the lungs. Messrs Allen and Pepys arrived at a similar conclusion; and since the appearance of their Essay, the opinion has prevailed very generally among physiologists, that in respiration the nitrogen of the air is altogether passive.

The facts ascertained by Dr Edwards relative to this subject are novel and of peculiar interest. This acute physiologist has reconciled the discordant results of preceding experimentalists, by showing that, during the respiration even of the same animal, the quantity of nitrogen may one while be increased, at another time diminished, and at a third wholly unchanged. He has traced these phenomena to the influence of the seasons; and he suspects, as indeed is most probable, that other causes, independently of season, have a share in their production. In nearly all the lower animals which were made the subjects of experiment, an augmentation of nitrogen was observable during summer. Sometimes, indeed, it was so slight that it might be disregarded. But in many other instances it was so great as to place the fact beyond the possibility of doubt; and on some occasions it almost equalled the whole bulk of the animal. Such continued to be the result of his inquiries until the close of October, when he observed a sensible diminution of nitrogen, and the same continued throughout the whole of winter and the beginning of spring.

There are two modes of accounting for these phenomena. According to one view, the nitrogen which disappears is ascribed to the ab-



sorption of what was inhaled, and its increase to direct exhalation, the opposite processes of absorption and exhalation being supposed not to occur at the same moment. According to the other view, both these processes are always going on at the same time, and the result depends on the preponderance of one over the other. When the absorption prevails, a smaller quantity of nitrogen is exhaled than was inspired; when the exhalation exceeds the absorption, an increase of nitrogen takes place; but when the absorption and exhalation are equal, the bulk of the inspired air, so far as nitrogen is concerned, does not undergo any change. The latter opinion, which is adopted by Dr Edwards, is supported by two decisive experiments performed by Messrs Allen and Pepys, in one of which a guinea-pig was confined in a vessel of oxygen gas, and in the other in an atmosphere composed of 21 measures of oxygen and 79 of hydrogen. In both cases the residual air contained a quantity of nitrogen greater than the bulk of the animal itself; and in the last a portion of hydrogen had disappeared. From this it follows that nitrogen may be exhaled from the lungs, and that hydrogen may be absorbed.

Two theories have been proposed in order to account for the phenomena of respiration. According to one theory, the carbonic acid found in the respired air is actually generated in the lungs themselves; while, according to the other, this gas is thought to exist ready formed in the blood, and to be merely thrown off from that liquid during its distribution through the lungs.

The former theory, which appears to have originated with Priestley, has received several modifications. Priestley imagined that the phenomena of respiration are owing to the disengagement of phlogiston from the blood, and its combination with the air. Dr Crawford modified this doctrine in the following manner. (Crawford on Animal Heat.) He was of opinion that venous blood contains a peculiar compound of carbon and hydrogen, termed *hydro-carbon*, the elements of which unite in the lungs with the oxygen of the air, forming water with the one, and carbonic acid with the other; and that the blood, thus purified, regains its florid hue, and becomes fit for the purposes of the animal economy.

The hypothesis of Crawford, however, is not merely liable to the objection that the supposed hydrocarbon, as respects the blood, is quite imaginary, but was found at variance with the leading facts established by Messrs Allen and Pepys. By the elaborate researches of these chemists it was established that carbonic acid gas contains its own volume of oxygen; and they also concluded that air, inhaled into the lungs, returns charged with a quantity of carbonic acid, almost exactly equal in bulk to the oxygen which disappears, an inference which, as applied to man and some of the lower animals, seems very near the truth. A review of these circumstances induced them to adopt the opinion that the oxygen of the air combines in the lungs exclusively with carbon; and that the watery vapour, which is always contained in the breath, is an exhalation from minute pulmonary vessels. They conceived that the fine animal membrane interposed between the blood and the air does not prevent chemical action from taking place between them.

This view has been further modified by Mr Ellis, who supposes that the carbon is separated from the venous blood by a process of secretion, and that then, coming into direct contact with oxygen, it is converted into carbonic acid. (Inquiry, &c. Parts. I. and II.)

The circumstance which led Mr Ellis to this opinion, was a disbelief in the possibility of oxygen acting upon the blood through the animal membrane in which it is confined. The experiments adduced in proof of the impermeability of membranous substances are not, however, quite satisfactory; while, on the contrary, the facts noticed by several accurate observers appear to leave no doubt that moist animal membranes, even in the living body, are in some way or other permeable to substances in a gaseous form\*.

According to the second theory, which was supported by La Grange and Hassenfratz, and has lately been adopted by Dr Edwards, carbonic acid, generated during the course of the circulation, is given off from the venous blood in the lungs, and oxygen gas is absorbed. This doctrine, though generally regarded hitherto as less probable than the preceding, is supported by very powerful arguments. The experiments and observations of Dr Edwards seem to leave no doubt that the blood, while circulating through the lungs, is capable of absorbing hydrogen, nitrogen, and oxygen gases, and of emitting nitrogen; and he has gone very far towards proving that the carbonic acid is derived from the same source. On confining frogs and snails for some time in an atmosphere of hydrogen, the residual air was found to contain a quantity of carbonic acid, which was in some instances even greater than the bulk of the animal; and a similar result was obtained with young kittens.

The confined limits of the present work do not admit of an examination into the respective advantages and disadvantages of these two theories. I shall merely observe, therefore, that, in the present stage of the inquiry, the deficiency of precise data prevents the establishment of one of them in preference to the other; but that the arguments preponderate in favour of the last.

The conversion of venous into arterial blood appears not to be confined to the lungs. The disengagement of carbonic acid from the surface of the skin, and the corresponding disappearance of oxygen gas was demonstrated by the experiments of Jurine and Abernethy; and although the accuracy of their results has been doubted by some persons, it has been confirmed by others. However this may be in the human subject, the fact with respect to many of the lower animals is unquestionable. Spallanzani proved that some animals possessed of lungs, such as serpents, lizards and frogs, produce the same changes on the air by means of their skin, as by their proper respiratory organs; and Dr Edwards, in a series of masterly experiments, has shown that this function compensates so fully for the want of respiration by the lungs, as to enable these animals, in the winter season, to live for an almost unlimited period under the surface of water.

### *On Animal Heat.*

The striking analogy between the processes of combustion and respiration, in both of which oxygen gas disappears, and an oxidized body is substituted for it, led Dr Black to infer that the caloric generated in the animal system, by means of which the more perfect ani-

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\* See some judicious remarks on this subject in the *Essay on Respiration and Animal Heat*, by Dr Williams, in the *Med. Chir. Trans. of Edinburgh*, vol. ii.

mals preserve their temperature above that of the surrounding medium, is derived from the changes going forward in the lungs. But this opinion is not founded on analogy alone; many circumstances conspire to show that the development of animal heat is dependent on the function of respiration, although the mode by which the effect is produced has not hitherto been satisfactorily determined. Thus, in all animals, whose respiratory organs are small and imperfect, and which therefore consume but a comparatively minute quantity of oxygen, and generate little carbonic acid, the temperature of the blood varies with that of the medium in which they live. In warm-blooded animals, on the contrary, in which the respiratory apparatus is larger, and the chemical changes more complicated, the temperature is almost uniform; and those have the highest temperature whose lungs, in proportion to the size of their bodies, are largest, and which consume the greatest quantity of oxygen. The temperature of the same animal at different times is connected with the state of the respiration. When the blood circulates sluggishly, and the temperature is low, the quantity of oxygen consumed is comparatively small; but, on the contrary, a large quantity of that gas disappears when the circulation is brisk, and the power of generating heat energetic. It has also been observed, especially by Crawford and De Laroche, that when an animal is placed in a very warm atmosphere, so as to require little heat to be generated within his own body, the consumption of oxygen is unusually small, and the blood within the veins retains the arterial character.

The connexion between the power of generating heat and respiration has been illustrated in a very pointed manner by Dr Edwards. Some young animals, such as puppies and kittens, require so small a quantity of oxygen for supporting life, that they may be deprived of that gas altogether for twenty minutes without material injury; and it is remarkable that so long as they possess this property, the temperature of their bodies sinks rapidly by free exposure to the air. But as they grow older they become able to maintain their own temperature, and at the same time their power to endure the privation of oxygen ceases. The same observation applies to young sparrows, and other birds which are naked when hatched; while young partridges, which are both fledged and able to retain their own temperature at the period of quitting the shell, die when deprived of oxygen as rapidly as an adult bird.

The first consistent theory of the production of animal heat was proposed by Dr Crawford. This theory was founded on the assumption that the carbonic acid contained in the breath is generated in the lungs, and that its formation is accompanied with the disengagement of caloric. But since the temperature of the lungs is not higher than that of other internal organs, and arterial very little if at all warmer than venous blood, it follows that the greater part of the caloric, instead of becoming free, must in some way or other be rendered insensible. Accordingly, on comparing the specific caloric of arterial and venous blood, Dr Crawford found the capacity of the former to exceed that of the latter in the ratio of 1030 to 892. He therefore inferred that the dark blood within the veins, at the moment of being arterialized, acquires an increase of insensible caloric; and that while circulating through the body, and gradually resuming the venous character, it suffers a diminution of capacity, and evolves a proportionate degree of heat.

Unfortunately, for the hypothesis of Crawford, one of the leading

facts on which it is founded has been called in question, Dr Davy maintaining, on the authority of his own experiments, that there is little or no difference between the capacities of venous and arterial blood. (Philos. Trans. for 1814.) If this be true, the hypothesis itself necessarily falls to the ground. One part of the doctrine of Crawford may, however, in a modified form, be applied to the theory of respiration advocated by Dr Edwards. For if oxygen be absorbed by the blood, in its passage through the lungs, and carbonic acid, ready formed, be emitted in return, it follows that this gas must be generated during the course of the circulation; and it may be inferred, that the heat developed in consequence of this chemical change, is at once communicated to the adjacent organs. In this way the question concerning the capacity of the blood for caloric may be entirely disregarded.

While some physiologists have been disposed to refer the source of animal heat entirely to the alternate changes of venous to arterial, and of arterial to venous blood, others have denied its agency altogether, ascribing the evolution of caloric solely to the influence of the nervous system. The chief foundation for this opinion is in the experiments of Mr Brodie, who inflated the lungs of animals recently killed by narcotic poisons or divisions of the spinal marrow. (Phil. Trans. for 1811 and 1812.) In an animal so treated, the blood continued to circulate, the phenomena of arterialization took place with regularity, oxygen gas disappeared, and carbonic acid was evolved; but notwithstanding the concurrence of all these circumstances, the temperature fell with equal, if not greater rapidity, than in another animal killed at the same time, but in which artificial respiration was not performed.

Were these experiments rigidly exact, they would lead to the opinion that no caloric is evolved by the mere process of arterialization. This inference, however, cannot be admitted for two reasons:—first, because other physiologists, in repeating the experiments of Brodie, have found that the process of cooling is retarded by artificial respiration; and, secondly, because it is difficult to conceive why the formation of carbonic acid, which uniformly gives rise to increase of temperature in other cases, should not be attended within the animal body with a similar effect. It may hence be inferred, that this is one of the sources of animal heat. It is certain, however, that the heat of animals cannot be maintained by the sole process of arterialization. Consistently with this fact, the researches of Dulong and Despretz agree in proving, in opposition to the results obtained by Lavoisier and Crawford, that a healthy animal imparts to surrounding bodies a quantity of heat considerably greater than can be accounted for by the combustion of the carbon thrown off during the same interval from the lungs, in the form of carbonic acid.

Though the influence of the nervous system over the development of animal heat is no longer doubtful, physiologists are not agreed as to the mode by which it operates. Its action may be either direct or indirect; that is, the nerves may possess some specific power of generating heat, or they may excite certain operations by which the same effect is occasioned. It is far from improbable, that the nerves act more by the latter than the former mode; that the infinite number of chemical phenomena going on in the minute arterial branches during the processes of secretion and nutrition, processes which are entirely dependent on the nervous system, are attended with the disengagement of caloric. This view has, at least, been ably defended by Dr Williams in the essay to which I have already referred.



## SECTION II.

## ON THE SECRETED FLUIDS SUBSERVIENT TO DIGESTION.

*Saliva, Pancreatic and Gastric Juices.*

*Saliva.*—The saliva is a slightly viscid liquor, secreted by the salivary glands. When mixed with distilled water, a flaky matter subsides, which is mucus, derived apparently from the lining membrane of the mouth. The clear solution, when exposed to the agency of galvanism, yields a coagulum, and is hence inferred by Mr Brande to contain albumen; but the quantity of this principle is so very small that its presence cannot be demonstrated by any other re-agent. The greater part of the animal matter remaining in the liquid is peculiar to the saliva, and may be termed *salivary matter*. It is soluble in water, insoluble in alcohol, and, when freed from the accompanying salts, is not precipitated by the sub-acetate of lead, corrosive sublimate, or by the infusion of nut-galls. The saliva likewise contains a small quantity of animal matter, which is soluble both in alcohol and water, and which is supposed by Tiedemann and Gmelin to be osmazome.

The solid contents of the saliva, according to Berzelius, do not exceed seven in 1000 parts, the rest being water. From the recent analysis of Tiedemann and Gmelin, the chief saline constituent is the muriate of potassa; but several other salts, such as the sulphate, phosphate, acetate, carbonate, and sulpho-cyanate of potassa, are likewise present in small quantity. The saliva of the human subject, according to the same authority, contains very little soda. The property which the saliva possesses of striking a red colour with a per-salt of iron is owing to the sulpho-cyanate of potassa. This acid exists also in the saliva of the sheep; but it has not been found in that of the dog. The saliva of the sheep contains so much carbonate of soda, that it effervesces with acids.

The only known use of the saliva is to form a soft pulpy mass with the food during mastication, so as to reduce it into a state fit for being swallowed with facility, and for being more readily acted on by the juices of the stomach.

*Pancreatic juice.*—This fluid is commonly supposed to be analogous to the saliva, but it appears from the analysis of Tiedemann and Gmelin that it is essentially different. The chief animal matters are albumen, and a substance like curd; but it also contains a small quantity of salivary matter and osmazome. It reddens litmus paper, owing to the presence of free acid, which is supposed to be the acetic. Its salts are nearly the same as those contained in the saliva, except that the sulpho-cyanic acid is wanting.

The uses of the pancreatic juice are entirely unknown.

*Gastric juice.*—The gastric juice collected from the stomach of an animal killed while fasting, is a transparent fluid which has a saline taste, and has neither an acid nor alkaline reaction. During the process of digestion, on the contrary, it is found to be distinctly acid. Thus free muriatic acid was detected under these circumstances by



Dr Prout\* in the stomach of the rabbit, hare, horse, calf, and dog; and he has discovered the same acid in the sour matter ejected from the stomachs of persons labouring under indigestion, a fact which has since been confirmed by Mr Children. Messrs Tiedemann and Gmelin have observed that the secretion of acid commences as soon as the stomach receives the stimulus of food or any foreign body. This effect is occasioned, for example, by the presence of flint stones or other indigestible matters; but it is produced in a still greater degree by substances of a stimulating nature. According to their observation the acidity is owing to the secretion of free muriatic and acetic acids.

The gastric juice coagulates milk, and it is generally supposed to produce this effect quite independently of the presence of an acid. According to the experiments of Spallanzani and Stevens it is highly antiseptic, not only preventing putrefaction, but rendering meat fresh after it is tainted. But of all the properties of the gastric juice, its solvent virtue is the most remarkable, being that on which depends the first stage of the process of digestion. When the food is introduced into the stomach, it is there intimately mixed with the gastric juice, by the agency of which it is dissolved, and converted into a semi-fluid matter called *chyme*. That this change is really owing to the solvent power of the gastric juice fully appears from the researches of Spallanzani, Reaumur, and Stevens. In the experiments of Dr Stevens, described in his Inaugural Dissertation, the common articles of food were inclosed in hollow silver spheres perforated with holes, and after remaining for some time within the stomach, completely protected from pressure and trituration, the alimentary substances were found to have been entirely dissolved. A similar effect takes place when nutritious matters, out of the body, are mixed with the gastric fluid, and the mixture is exposed to a temperature of 100° Fahr. So great, indeed, is the solvent power of this fluid, that it has been known to dissolve the coats of the stomach itself; at least the corrosions of this organ sometimes witnessed in persons who have died suddenly while fasting, and in good health, were ascribed by the celebrated physiologist, John Hunter, to this cause.

No department of chemical physiology is more obscure than that of digestion. There appears so little connexion between the properties and composition of the gastric juice, that physiologists are quite at a loss in what way to account for its solvent power. An attempt has lately been made by Tiedemann and Gmelin to explain the phenomena on chemical principles. They ascribe its solvent action to the dilute muriatic and acetic acids, which are always secreted during the digestive process, and which, according to their observation, are capable of dissolving most or all of the substances employed as food. They have not shown, however, that the gastric juice in its neutral state, or when neutralized by an alkali, is devoid of solvent properties, a circumstance which requires investigation before a decisive opinion can be formed of the accuracy of their views.

### *Bile and Biliary Concretions.*

The bile is a yellow or greenish-yellow coloured fluid, of a peculiar sickening odour, and of a taste at first sweet and then bitter, but ex-

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\* Philosophical Transactions for 1824.

ceedingly nauseous. Its consistence is variable, being sometimes limpid, but more commonly viscid and ropy. It is rather denser than water, and may be mixed with that liquid in every proportion. It contains a minute quantity of free soda, and is therefore slightly alkaline; but owing to the colour of the bile itself, its action on test paper is scarcely visible.

Of the chemists who have of late years investigated the composition of the bile, Thénard, Berzelius, and Tiedemann and Gmelin deserve particular mention. In an elaborate essay published in the *Mémoires d'Arcueil*, vol. i. Thénard endeavoured to show, that the bile of the ox consists of three distinct animal principles, a yellow colouring matter, a species of resin, and a peculiar substance, to which, from its sweetish bitter taste, he has applied the name of *picromel*. According to his analysis, 800 parts of bile consist of water 700 parts, resin 15, picromel 69, yellow matter about 4, soda 4, phosphate of soda 2, muriates of soda and potassa, 3.5, sulphate of soda 0.8, phosphate of lime and perhaps magnesia 1.2, and a trace of the oxide of iron. He supposed the resin to be combined with the picromel and soda, and ascribes its solubility in water to this cause.

Berzelius takes a totally different view of the constitution of the bile. He denies that this fluid contains any resinous principle, and regards the yellow matter, resin, and picromel of Thénard, as one and the same substance, to which he applies the name of *Biliary matter*. (Med. Chir. Trans. vol. iii.) Tiedemann and Gmelin, however, in their recent work on Digestion, admit the existence of picromel and resin as the chief constituents of bile; although it appears from their experiments that the substance described by Thénard as Picromel, was not pure, but contained a portion of resin. According to the analysis of these chemists, the bile of the ox is a very complex fluid, consisting of the following ingredients:—water to the extent of 91.5 per cent.; a volatile odoriferous principle; cholesterine; resin; asparagin; picromel; yellow colouring matter; a peculiar azotized substance, soluble in water and alcohol; a substance which is soluble in hot alcohol, but insoluble in water, supposed to be gliadine; osmazome; a principle which emits an urinous odour when heated; a substance analogous to albumen or caseous matter; and mucus. The salts of the bile are the margarate, oleate, acetate, *cholate*, bicarbonate, phosphate, sulphate, and muriate of soda, together with a little phosphate of lime. The *cholic* is a peculiar animal acid, which crystallizes in needles, reddens litmus paper, and is distinguished from analogous compounds by having a sweet taste.

The flaky precipitate which is occasioned by adding acids to bile from the ox, consists of several substances. At first the caseous and colouring matters, along with mucus, are thrown down; and, afterwards, the margaric acid, and a compound of picromel and resin with the acid employed, are precipitated. When the acetate of lead is mixed with this fluid, a white precipitate falls, which consists of the oxide of lead combined with the phosphoric, sulphuric, and several other acids, together with a small quantity of the compound of picromel and resin. On adding the subacetate of lead to the clear liquid, a copious precipitate ensues, consisting chiefly of picromel, resin, and the oxide of lead. If this compound is suspended in water, through which a current of sulphuretted hydrogen gas is transmitted, the sulphuret of lead and the resin subside, while the picromel remains in solution. By collecting and drying the precipitate, and digesting it in

alcohol, the resin is dissolved, and may be obtained by evaporation. The aqueous solution, when evaporated, yields the picromel of Thénard; but according to Tiedemann and Gmelin, it still contains a portion of resin. The chief difficulty, indeed, of preparing pure picromel arises from its tendency to dissolve the resin, and the only mode of separating them is by throwing them down repeatedly with the subacetate of lead. By this process, the affinity of the picromel and resin for each other is gradually lessened, until at length the separation is rendered complete.

Pure picromel occurs in opaque rounded crystalline particles, is soluble in water and alcohol, but is insoluble in ether. Its taste is sweet without any bitterness; but it cannot be regarded as a species of sugar, because a large quantity of nitrogen enters into its composition. Its aqueous solution is not precipitated by acids, or by the acetate and sub-acetate of lead. When digested with the resin of the bile, a portion of the latter is dissolved, and a solution is obtained, which has both a bitter and a sweet taste, and yields a precipitate with the subacetate of lead and the stronger acids. This is the compound which causes the peculiar taste of the bile.

The bile of the human subject has not been studied so minutely as that of the ox. According to Thénard it consists, besides salts, of water, colouring matter, albumen, and a species of resin. M. Chevallier has since detected picromel, and M. Chevreul cholesterine, in human bile; and both these discoveries have been confirmed by the observations of Tiedemann and Gmelin.

The derangement which takes place in the system when the secretion of bile or its passage into the intestines is arrested, is a sufficient indication of the importance of this fluid. It acts as a stimulus to the intestinal canal generally, and produces on the chyme some peculiar change, which is essential to its conversion into chyle.

*Biliary Calculi.*—The concretions which are sometimes formed in the human gall-bladder have been particularly examined by Fourcroy, Thénard, and Chevreul. Fourcroy found that they consist chiefly of a peculiar fatty matter, resembling spermaceti, which he has included under the name of *adipocire*; (page 425) and the experiments of Thénard tended to confirm this view. According to M. Chevreul, however, biliary concretions in general are composed of the yellow colouring matter of the bile and cholesterine, the latter predominating, and being sometimes in a state of purity; and I have had frequent opportunities of satisfying myself of the accuracy of this observation\*. These substances may easily be separated from each other by boiling alcohol, which dissolves the cholesterine and leaves the colouring matter; or by digestion in dilute potassa, in which the colouring matter is dissolved, and the cholesterine insoluble.

Gall-stones sometimes contain a portion of inspissated bile; and in some rare instances the cholesterine is entirely wanting.

The concretions found in the gall-bladder of the ox consist almost entirely of the yellow biliary colouring matter, which, from the beauty and permanence of its tint, is much valued by painters. This substance is readily distinguished by its yellow or brown colour, by inso-

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\* See an interesting case of gall-stone described by Dr Craigie in the Edinburgh Medical and Surgical Journal for 1824.

lubility in water and alcohol, and by being readily dissolved by a solution of potassa. The solution has at first a yellowish-brown colour, which gradually acquires a green tint, and is precipitated in green flocks by muriatic acid. According to the observations of Tiedemann and Gmelin the colouring matter is influenced by the presence of oxygen gas. The yellowish precipitate, occasioned by adding muriatic acid to bile, absorbs oxygen by exposure to the air, and its colour changes to green. The action of nitric acid is still more remarkable. By successive additions of this acid, the tint of the colouring matter may be converted into green, blue, violet and red in the course of a few seconds.

*Erythrogen*.—This substance was discovered in 1821 by M. Bizio of Venice, in a peculiar fluid, quite different from bile, which was found in the gall-bladder of a person who had died of jaundice. It is of a green colour, transparent, tasteless, and of the odour of putrid fish. It is unctuous to the touch, may be scratched or cut with facility, and has a specific gravity of 1.57. It does not affect the colour of litmus or turneric paper. At 110° F. it fuses, having the appearance of oil, and crystallizes when slowly cooled; and at 122° F. it rises in the form of vapour. It is insoluble in water and ether, but is dissolved readily by hot alcohol; and the solution, by partial evaporation and cooling, yields crystals in the form of rhomboidal parallelopipeds.

When erythrogen is put into nitric acid of the temperature of about 120° or 140° Fahr. its green tint disappears, effervescence, owing to the escape of oxygen gas, ensues, and the solution acquires a deep purple colour. A similar phenomenon takes place, with disengagement of hydrogen gas, when erythrogen is digested in a solution of ammonia; and when volatilized in the open air, it yields a purple coloured vapour. M. Bizio is of opinion that the erythrogen, under all these circumstances, unites with nitrogen, and that the product is identical with the colouring matter of the blood. The production of the red compound is characteristic of erythrogen, and suggested the name by which this substance is designated (*Eρυθρος ruber*). (*Journal of Science*, vol. xvi.)

Erythrogen has not been discovered either in bile or in any of the animal fluids.

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## SECTION III.

### CHYLE.—MILK.—EGGS.

*Chyle*.—The fluid absorbed by the lacteal vessels from the small intestines during the process of digestion, is known by the name of *chyle*. Its appearance varies in different animals; but as collected from the thoracic duct of a mammiferous animal three or four hours after a meal, it is a white opaque fluid like milk, having a sweetish and slightly saline taste. In a few minutes after removal from the duct it becomes solid, and in the course of twenty-four hours separates into a firm coagulum, and a limpid liquid, which may be called the serum of the chyle. The coagulum is an opaque white substance, of a

slightly pink hue, insoluble in water, but soluble easily in the alkalies and alkaline carbonates. Vauquelin\* regards it as fibrin in an imperfect state, or as intermediate between that principle and albumen; but Mr Brande† considers it more closely allied to the caseous matter of milk than to fibrin.

The serum of chyle is rendered turbid by heat, and a few flakes of albumen are deposited; but when boiled after being mixed with acetic acid, a copious precipitation ensues. To this substance, which thus differs slightly from albumen, Dr Prout has applied the name of *incipient albumen*. The same chemist has made a comparative analysis of the chyle of two dogs, one of which was fed on animal and the other on vegetable substances, and the result of his inquiry is as follows:—(Annals of Philos. vol. xiii. p. 25.)

	<i>Vegetable Food.</i>	<i>Animal Food.</i>
Water, . . . . .	93.6	89.2
Fibrin, . . . . .	0.6	0.8
Incipient Albumen? . . . . .	4.6	4.7
Albumen with a little red colouring matter, . . . . .	0.4	4.6
Sugar of milk? . . . . .	a trace	—
Oily matter, . . . . .	a trace	a trace
Saline matters, . . . . .	0.8	0.7
	<hr/> 100.0	<hr/> 100.0

*Milk*.—This well known fluid, secreted by the females of the class *mammalia* for the nourishment of their young, consists of three distinct parts, the cream, curd, and whey, into which by repose it spontaneously separates. The cream, which collects upon its surface, is an unctuous, yellowish-white opaque fluid, of an agreeable flavour. According to Berzelius, 100 parts of cream, of specific gravity 1.0244, consist of butter 4.5, caseous matter 3.5, and whey 92. By agitation, as in the process of churning, the butter assumes the solid form, and is thus obtained in a separate state. During the operation there is an increase of temperature amounting to about three or four degrees, oxygen gas is absorbed, and an acid is generated; but the absorption of oxygen cannot be an essential part of the process, since butter may be obtained by churning, even when the atmospheric air is entirely excluded.

After the cream has separated spontaneously, the milk soon becomes sour, and gradually separates into a solid coagulum called curd, and a limpid fluid which is whey. This coagulation is occasioned by free acetic acid, and it may be produced at pleasure either by adding a free acid, or by means of the fluid known by the name of *rennet*, which is made by infusing the inner coat of a calf's stomach in hot water. When an acid is employed, the curd is found to contain some of it in combination, and may therefore be regarded as an insoluble compound of an acid with the caseous matter of milk; but nothing certain is known respecting the mode by which the gastric fluid, the active principle of rennet, produces its effect.

The curd of skim milk, made by means of rennet, and separated from the whey by washing with water, is *caseous matter*, or the basis

\* An. de Ch. vol. lxxxi.

† Philos. Trans. for 1812.



of cheese, in a state of purity. It is a white, insipid, inodorous substance, insoluble in water, but readily soluble in the alkalies, especially in ammonia. By alcohol it is converted, like albumen and fibrin, into an adipocirous substance of a fetid odour; and, like the same substances, it may be dissolved by a sufficient quantity of acetic acid.

Caseous matter has considerable analogy to albumen, especially in being coagulated by acids. It is not coagulated, however, by heat; although the tendency to undergo this change is indicated by the film which forms upon the surface of heated milk, an effect apparently connected with exposure to the air. It differs also from albumen in the nature of the spontaneous changes to which it is subject. When kept in a moist state it undergoes a species of fermentation precisely analogous to that experienced by gluten under the same circumstances. (Page 397.) The characteristic flavour of cheese is ascribed by Proust to the presence of the caseate of ammonia. (Proust in the *An. de Ch. et de Ph.* vol. x.)

According to the analysis of Gay-Lussac and Thénard, 100 parts of the caseous matter are composed of carbon 59.781, hydrogen 7.429, oxygen 11.409, and nitrogen 21.381. It yields by incineration a white ash amounting to 6.5 per cent of its weight, the greater part of which is phosphate of lime, a circumstance which renders caseous matter an article of food peculiarly proper for young animals.

Milk carefully deprived of its cream has a specific gravity of about 1.033; and 1000 parts of it, according to Berzelius, are thus constituted:—water 928.75, caseous matter with a trace of butter 28; sugar of milk 35; muriate and phosphate of potassa 1.95; lactic (acetic) acid, acetate of potassa and a trace of lactate of iron 6.00; and earthy phosphates 0.30. Subtracting the caseous matter, the remaining substances constitute whey.

*Eggs.*—The composition of the recent egg and the changes which it undergoes during the process of incubation, have been ably investigated by Dr Prout. (*Phil. Trans.* for 1822.) New-laid eggs are rather heavier than water; but they become lighter after a time, in consequence of water evaporating through the pores of the shell, and air being substituted for it. An egg of ordinary size yields to boiling water about three-tenths of a grain of saline matter, consisting of the sulphates, carbonates, and phosphates of lime and magnesia, together with animal matter and a little free alkali.

Of an egg which weighs 1000 grains, the shell constitutes 106.9, the white 604.2. and the yelk 288.9 grains. The shell contains about two per cent. of animal matter, one per cent. of the phosphates of lime and magnesia, and the residue is carbonate of lime with a little carbonate of magnesia.

When the yelk of a hard boiled egg is repeatedly digested in alcohol of specific gravity 0.807, until that fluid comes off colourless, there remains a white pulverulent residuum, possessed of many of the properties of albumen, but distinguished from that principle by containing a large quantity of phosphorus in some unknown state of combination. The alcoholic solution is of a deep yellow colour, and on cooling deposits crystals of a sebaceous matter, and a portion of yellow semi-fluid oil. On distilling off the alcohol, the oil is left in a separate state. When the yelk is dried and burned, the phosphorus is converted into phosphoric acid, which, melting into a glass upon the surface of the charcoal, protects it from complete combustion. In the white of the egg, which consists chiefly of albumen, sulphur is present.

The obvious use of the phosphorus contained in the yolk is to supply phosphoric acid for forming the bones of the chick ; but Dr Prout was unable to discover any source of the lime with which that acid unites to form the earthy part of bone. It cannot be discovered in the soft parts of the egg ; and hitherto no vascular connexion has been traced between the chick and its shell.

## SECTION IV.

### ON THE LIQUIDS OF SEROUS AND MUCOUS SURFACES, &c. AND ON PURULENT MATTER.

The surface of the cellular membrane is moistened with a peculiar limpid transparent fluid called *lymph*, which is in very small quantity during health, but collects abundantly in some dropsical affections. Mr Brande collected it from the thoracic duct of an animal which had been kept without food for twenty-four hours. Its chief constituent is water, besides which it contains muriate of soda and albumen, the latter being in such minute quantity that it is coagulated only by the action of galvanism. Lymph does not affect the colour of test paper ; but when evaporated to dryness, the residue gives a green tint to the syrup of violets.

The fluid secreted by the serous membranes in general, such as the pericardium, pleura, and peritoneum, is very similar to lymph. According to Dr Bostock, 100 parts of the liquid of the pericardium consist of water 92 parts, albumen 5.5, mucus 2, and muriate of soda 0.5. The serous fluid exhaled within the ventricles of the brain in *Hydrocephalus internus* is composed, in 1000 parts, of water 988.3, albumen 1.66, muriate of potassa and soda 7.09, lactate (acetate) of soda and its animal matter 2.32, soda 0.28, and animal matter soluble only in water, with a trace of phosphates 0.35. (Berzelius, in *Med. Chir. Trans.* vol. iii. p. 252.)

The liquor of the amnios, or the fluid contained in the membrane which surrounds the *fœtus in utero*, differs in different animals. That of the human female was found by Vauquelin and Buniva to contain a small quantity of albumen, soda, muriate of soda, phosphate and carbonate of lime, and a matter like curd which gives it a milky appearance. That of the cow, according to the same authority, contains the substance already described under the name of amniotic acid ; but several other chemists, such as Prout, Dulong and Labillardière, and Lassaigne, have been unable to detect it. M. Lassaigne states, that this acid exists in the fluid of the allantois of the cow. Dr Prout found some sugar of milk in the amnios of a woman. (*An. of Phil.* vol. v. p. 417.)

*Humours of the Eye.*—The aqueous and vitreous humours of the eye contain rather more than 80 per cent. of water. The other constituents are a small quantity of albumen, muriate and acetate of soda, pure soda, though scarcely sufficient to affect the colour of test paper, and animal matter soluble only in water, but which is not gelatine. (Berzelius.) The crystalline lens, besides the usual salts, contains 36 per cent. of a peculiar animal matter, very analogous to albumen, if not identical with it. In cold water it is soluble, but is coagu-

lated by boiling. The coagulum, according to Berzelius, has all the properties of the colouring matter of the blood excepting its colour.

The tears are limpid and of a saline taste, dissolve freely in water, and, owing to the presence of free soda, communicate a green tint to the blue infusion of violets. Their chief salts are the muriate and phosphate of soda. According to Fourcroy and Vauquelin the animal matter of the tears is mucus; but it is more probably either albumen, or some analogous principle. Its precise nature has not however been satisfactorily determined.

*Mucus*.—The term *mucus* has been employed in very different significations. Dr Bostock applies it to a peculiar animal matter which is soluble both in hot and cold water, is not precipitated by corrosive sublimate or solution of tannin, is not capable of forming a jelly, and which yields a precipitate with the sub-acetate of lead.

The existence of this principle has not, however, been fully established; for the presence of muriatic and phosphoric acids, the latter of which is frequently contained in animal fluids, and the former scarcely ever absent, sufficiently accounts for the precipitates occasioned in them by the salts of lead or silver. But even supposing the opinion of Dr Bostock to be correct, it would be advisable to give some new name to his principle, and apply the term *mucus* solely to the fluid secreted by mucous surfaces.

The properties of *mucus* vary somewhat according to the source from which it is derived; but its leading characters are in all cases the same, and are best exemplified in *mucus* from the nostrils. Nasal *mucus*, according to Berzelius, has the following properties. Immersed in water, it imbibes so much of that fluid as to become transparent, with the exception of a few particles which remain opaque. When dried on blotting paper, it loses its transparency, but again acquires it when moistened. It is not coagulated or rendered horny by being boiled in water; but as soon as the ebullition has ceased, it collects unchanged at the bottom of the vessel. It is dissolved by dilute sulphuric acid. Nitric acid at first coagulates it; but by continued digestion, the *mucus* at first softens and is finally dissolved, forming a clear yellow liquid. Acetic acid hardens *mucus*, and does not dissolve it even at a boiling temperature. Pure potassa at first renders it more viscid, but afterwards dissolves it. By tannin *mucus* is coagulated, both when softened by the absorption of water, and when dissolved either in acid or an alkali.

*Pus*.—Purulent matter is the fluid secreted by an inflamed and ulcerated surface. Its properties vary according to the nature of the sore from which it is discharged. The purulent matter formed by an ill-conditioned ulcer is a thin, transparent, acrid, fetid ichor; whereas a healing sore in a sound constitution yields a yellowish-white coloured liquid, of the consistence of cream, which is described as bland, opaque, and inodorous. This is termed healthy *pus*, and is possessed of the following properties. Though it appears homogeneous to the naked eye, when examined with the microscope it is found to consist of minute globules floating in a transparent liquid. Its specific gravity is about 1.03. It is insoluble in water; and is thickened, but not dissolved by alcohol. When recent it does not affect the colour of test paper; but by exposure to the air it becomes acid. The dilute acids have little effect upon it; but strong sulphuric, nitric, and muriatic acids dissolve it, and the *pus* is thrown down by dilution with water. Ammonia reduces it to a transparent jelly, and gradually dis-

solves a considerable portion of it. With the fixed alkalies it forms a whitish ropy fluid, which is decomposed by water.

The composition of pus has not been ascertained with precision; but its characteristic ingredient is more closely allied to albumen than to the other animal principles.

Several attempts have been made to discover a chemical test for distinguishing pus from mucus. When these fluids are in their natural state, the appearance of each is so characteristic that the distinction cannot be attended with any difficulty; but, on the contrary, when a mucous surface is inflamed, its secretion becomes opaque, and, as sometimes happens in some pulmonary diseases, acquires more or less of the aspect of pus. Mr Charles Darwin, who examined this subject, pointed out three grounds of distinction between them. 1. When the solution of these liquids in sulphuric acid is diluted, the pus subsides to the bottom, and the mucus remains suspended in the water. 2. When pus and catarrhal mucus are diffused through water, the former sinks, and the latter floats. 3. Pus is precipitated from its solution in potassa by water, while the solution of mucus is not decomposed by similar treatment. Dr Thomson, in his system of chemistry, has given the following test on the authority of Grassmeyer. The substance to be examined, after being triturated with its own weight of water, is mixed with an equal quantity of a saturated solution of the carbonate of potassa. If it contain pus, a transparent jelly forms in a few hours; but this does not happen if mucus only is present. Dr Young, in his work on Consumptive Diseases, has given a very elegant character for distinguishing pus, founded on its optical properties. But the practical utility of tests of any kind is rendered very questionable by the fact that inflamed mucous membranes may secrete genuine pus without breach of surface, and that the natural passes into purulent secretion by insensible shades.

*Sweat.*—Watery vapour is continually passing off by the skin in the form of insensible perspiration; but when the external heat is considerable, or violent bodily exercise is taken, drops of fluid collect upon the surface, and constitute what is called sweat. This fluid consists chiefly of water; but it contains some muriate of soda and free acetic acid, in consequence of which it has a saline taste and an acid reaction.

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## SECTION V.

### *ON THE URINE AND URINARY CONCRETIONS.*

The urine differs from most of the animal fluids which have been described by not serving any ulterior purpose in the animal economy. It is merely an excretion designed for ejecting from the system substances, which by their accumulation within the body would speedily prove fatal to health and life. The sole office of the kidneys, indeed, appears to consist in separating from the blood the superfluous matters that are not required or adapted for nutrition, or which have already formed a part of the body, and been removed by absorption. The substances which in particular pass off by this organ are nitrogen, in the form of highly azotized products, and various saline and earthy

compounds. This sufficiently accounts for the great diversity of different substances contained in the urine.

The quantity of the urine is affected by various causes, especially by the nature and quantity of the liquids received into the stomach; but on an average a healthy person voids between thirty and forty ounces daily. The quality of this fluid is likewise influenced by the same circumstances, being sometimes in a very dilute state, and at others highly concentrated. The urine voided in the morning by a person who has fed heartily, and taken no more fluids than is sufficient for satisfying thirst, may be regarded as affording the best specimen of natural healthy urine.

The urine in this state is a transparent limpid fluid of an amber colour, having a saline taste, and while warm emitting an odour, which is slightly aromatic, and not all disagreeable. Its specific gravity in its most concentrated form, is about 1.030. It gives a red tint to litmus paper, a circumstance which indicates the presence either of a free acid or of a super-salt. Though at first quite transparent, an insoluble matter is deposited on standing; so that urine voided at night is found to have a light cloud floating in it by the following morning. This substance consists in part of mucus from the urinary passages, and partly of the super-urate of ammonia, which is much more soluble in warm than in cold water.

The urine is very prone to spontaneous decomposition. When kept for two or three days it acquires a strong urinous smell; and as the putrefaction proceeds, the disagreeable odour increases, until at length it becomes exceedingly offensive. As soon as these changes commence, the urine ceases to have an acid reaction, and the earthy phosphates are deposited. In a short time, a free alkali makes its appearance, and a large quantity of the carbonate of ammonia is gradually generated. Similar changes may be produced in recent urine by continued boiling. In both cases the phenomena are owing to the decomposition of urea, which is almost entirely resolved into carbonate of ammonia.

The composition of the urine has been studied by several chemists, but the most recent and elaborate analysis of this fluid is by Berzelius. According to the researches of this indefatigable chemist, 1000 parts of urine are composed of

Water,	933.00
Urea,	30.10
Uric acid,	1.00
Free lactic acid, lactate of ammonia, and animal matter not separable from them,	17.14
Mucus of the bladder,	0.32
Sulphate of potassa,	3.71
Sulphate of soda,	3.16
Phosphate of soda,	2.94
Phosphate of ammonia,	1.65
Muriate of soda,	4.45
Muriate of ammonia,	1.50
Earthy matters, with a trace of fluete of lime,	1.00
Siliceous earth,	0.03

Besides the ingredients included in the preceding list, the urine contains several other substances in small quantity. From the property this fluid possesses of blackening silver vessels in which it is



evaporated, owing to the formation of the sulphuret of silver, Proust inferred the presence of unoxidized sulphur; and Dr Prout, from the odour of phosphuretted hydrogen, which he thinks he has perceived in putrefying urine, suspects that phosphorus is likewise present. The urine also contains a peculiar yellow colouring matter, which has not hitherto been obtained in a separate state. From the precipitate occasioned in urine by the infusion of gall-nuts, the presence of gelatine has been inferred; but this effect appears owing to the presence not of gelatine but of a small portion of albumen.

According to Scheele, the urine of infants sometimes contains benzoic acid, a compound which, when present, may be easily procured by evaporating the urine nearly to the consistence of syrup, and adding muriatic acid. The precipitate, consisting of uric and benzoic acids, is digested in alcohol, which dissolves the benzoic acid.

Notwithstanding the high authority of Berzelius, it is very doubtful if any free acid be present in healthy urine. Dr Prout, with every appearance of justice, maintains that the acidity of recent urine is occasioned by super-salts, and not by uncombined acid. He is of opinion that the acid reaction is chiefly, if not wholly, to be ascribed to the super-phosphate of lime and super-urate of ammonia, salts which he finds may co-exist in a liquid without mutual decomposition. A very strong argument, which to me indeed appears conclusive, in favour of this view, is derived from the fact, that on adding muriatic acid to recent urine, minute crystals of uric acid are gradually deposited, as always happens when this acid subsides slowly from a state of solution; but, on the contrary, if no free acid is added, an amorphous sediment, which Dr Prout regards as the super-urate of ammonia, is obtained.

Such is a general view of the composition of human urine in its natural healthy state. But this fluid is subject to a great variety of morbid conditions, which arise either from the deficiency or excess of certain principles which it ought to contain, or from the presence of others wholly foreign to its composition. As the study of these affections affords an interesting example of the application of chemistry to pathology and the practice of medicine, I shall mention briefly some of the most important morbid states of this fluid, referring for more ample details to the excellent treatise of Dr Prout\*.

Of the substances which, though naturally wanting, are sometimes contained in the urine, the most remarkable is sugar, which is secreted by the kidneys in diabetes. (Page 419.) Diabetic urine has a sweet taste, and yields a syrup by evaporation, is almost always of a pale straw colour, and in general has a greater specific gravity than ordinary urine. It contains a remarkable small proportion of azotized substances, so that it has no tendency to putrefy; but the presence of sugar renders it susceptible of undergoing the vinous fermentation.

The acidifying process which is constantly going forward in the kidneys, as evinced by the formation of sulphuric, phosphoric, and uric acids, sometimes proceeds to a morbid extent, in consequence of which two acids, the oxalic and nitric, are generated, neither of which exists in healthy urine. The former, by uniting with lime, gives rise to one of the worst kinds of urinary concretions; and the latter, in the

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\* Inquiry into the Nature and Treatment of Gravel, Calculus, &c.

opinion of Dr Prout, leads to the production of the purpurate of ammonia, by reacting on the uric acid.

In severe cases of jaundice the bile passes from the blood into the kidneys, and communicates a yellow colour to the urine. The most delicate test of its presence is muriatic acid, which causes a green tint.

Though albumen is contained in very minute quantity in healthy urine, in some diseases it is present in large proportion. According to Dr Blackall it is characteristic of certain kinds of dropsy, accompanied with an inflammatory diathesis, as in that which supervenes on scarlet fever; and Dr Prout has described two cases of albuminous urine, in which, without any febrile symptoms, albumen existed in such quantity that spontaneous coagulation took place within the bladder.

In certain states of the system urea is generated in an unusually small proportion. This occurs especially in *diabetes mellitus*, and in acute and chronic inflammation of the liver, diseases in which urea is said sometimes to be wholly wanting; but the experience of Dr Prout has led him to doubt if it is ever entirely absent. Dr Henry has shown that urea, when mixed with a considerable proportion of sugar, cannot be discovered by the usual test of nitric acid; and, consequently, that though present in diabetic urine, it might easily be overlooked. The method by which he has succeeded in detecting it in such cases is by distillation, urea being the only known animal principle which is converted into carbonate of ammonia at a boiling temperature. (Med. Chir. Trans. vol. ii. p. 127.) During the hysteric paroxysm, also, the animal matters of the urine are deficient, while its saline ingredients are secreted in unusual quantity. An excess of urea occasionally exists. The mode by which Dr Prout estimates the proportion of this principle is by putting the urine in a watch glass, and carefully adding to it nearly an equal quantity of nitric acid, in such a manner that the acid may collect at the bottom. If spontaneous crystallization ensue, an excess of urea is indicated; and the degree of excess may be inferred approximatively by marking the time which elapses before the effect takes place. Undiluted healthy urine yields crystals only after an interval of half an hour; but the nitrate crystallizes within that interval when the urea is in excess.

An unusually abundant secretion of uric acid is a circumstance by no means uncommon. In some instances this acid makes its appearance in a free state; but happily it generally occurs in combination with an alkali, especially with soda or ammonia. As the urates are much more soluble in warm than in cold water, the urine in which they abound is quite clear at the moment of being voided, but deposits a copious sediment in cooling. The undue secretion of these salts, if temporary, occasions scarcely any inconvenience, and arises from such slight causes, that it frequently takes place without being noticed. This affection is generally produced by errors in diet, whether as to quantity or quality, and by all causes which interrupt the digestive process in any of its stages, or render it imperfect. Dr Prout specifies unfermented heavy bread, and hard boiled puddings or dumplings, as in particular disposing to the formation of the urates. These sediments have commonly a yellowish tint, which is communicated by the colouring matter of the urine; or when they are deposited in fevers, forming the lateritious sediment, they are red, in consequence of the colouring matter of the urine being then more abundant. In fevers of an irritable nature, as in hectic, the sediment has a pink co-

lour, which is ascribed by Dr Prout to the presence of the purpurate of ammonia, and by Proust to the rosacic acid. (Page 421.)

So long as the uric acid remains in combination with a base, it never yields a crystalline deposit; but when this acid is in excess and in a free state, its very sparing solubility causes it to separate in minute crystals, even within the bladder, giving rise to two of the most distressing complaints to which human nature is subject,—to gravel when the crystals are detached from one another, and when agglutinated by animal matter into concrete masses, to the disease called stone. These diseases may arise either from uric acid being directly secreted by the kidneys, or, as Dr Prout suspects, from the formation of some other acid, by which the urate of ammonia is decomposed. The tendency of the urine to contain free acid occurs most frequently in dyspeptic persons of a gouty habit, and is familiarly known by the name of the uric or lithic acid diathesis. In these individuals the disposition to undue acidity of the urine is superadded to that state of the system which leads to an unusual supply of the urates.

A deficiency of acid in the urine is not less injurious than its excess. As the phosphate of lime in its neutral state is insoluble in water, this salt cannot be dissolved in the urine except by being in the form of a superphosphate. Hence it happens that healthy urine yields a precipitate, when it is neutralized by an alkali; and if, by the indiscriminate employment of alkaline medicines, or from any other cause, the urine, while yet within the bladder, is rendered neutral, the earthy phosphates are necessarily deposited, and an opportunity afforded for the formation of a stone.

### *Urinary Concretions.*

The first step towards a knowledge of urinary calculi was made in the year 1776 by Scheele, who showed that many of the concretions formed in the bladder consist of uric or lithic acid. The subject was afterwards successfully investigated by Drs Wollaston and Pearson in this country, and by Fourcroy and Vauquelin in France; but the honour of having first ascertained the composition and chemical characters of most of the species of urinary calculi at present known, belongs to Dr Wollaston. (Phil. Trans. for 1797.) The chemists who have since materially contributed to advance our knowledge of this department of science, are Dr Henry, Mr Brande, Dr Prout, and the late Dr Marcet, to whose "Essay on the Chemical History and Medical Treatment of Calculous Disorders," I may refer the reader who is desirous of studying this important subject.

The most common kinds of urinary concretions may be conveniently divided into six species: 1. The uric acid calculus; 2. The bone earth calculus, principally consisting of the phosphate of lime; 3. The ammoniaco-magnesian phosphate; 4. The fusible calculus, being a mixture of the two preceding species; 5. The mulberry calculus, composed of the oxalate of lime; and, lastly, The cystic oxide calculus. (Marcet.)

1. The uric acid forms a hard inodorous concretion, commonly of an oval form, of a brownish or fawn colour, and smooth surface. These calculi consist of layers arranged concentrically around a central nucleus, the laminæ being distinguished from each other by a slight difference in colour, and sometimes by the interposition of some other substance.

This species is readily distinguished by the following characters. It is very sparingly soluble in water and muriatic acid. Digested in pure potassa it quickly disappears, and on adding an acid to the solution, the uric acid is precipitated. It is dissolved with effervescence by nitric acid, and the solution yields the purpurate of ammonia when evaporated. Before the blowpipe it becomes black, emits a peculiar animal odour, and is gradually consumed, leaving a trace of white ash, which has an alkaline reaction.

As a variety of this species, may be mentioned the urate of ammonia, a rare kind of calculus first noticed by Fourcroy. Mr Brande and Dr Marcet expressed a doubt of its ever forming an independent concretion, but its existence, as such, has been established by Dr Prout. The urate of ammonia has the same general chemical character as the uric acid, from which it is distinguished by its solubility in boiling water, when reduced to powder, and by its solution in potassa being attended with the disengagement of ammonia. It deflagrates remarkably before the blowpipe. (Med. Chir. Trans. vol. x. p. 389.)

2. The bone earth calculus, first correctly analyzed by Dr Wollaston, consists of the phosphate of lime. The surface of these calculi is of a pale brown colour, and quite smooth as if they had been polished. When sawed through the middle, they are found to be laminated in a very regular manner, and the layers in general adhere so slightly that they may be separated with ease into concentric crusts.

This calculus, when reduced to powder, dissolves with facility in dilute nitric or muriatic acid, but is insoluble in potassa. Before the blowpipe it first assumes a black colour, from the decomposition of a little animal matter, and then becomes quite white, undergoing no further change unless the heat be very intense, when it is fused.

3. The phosphate of ammonia and magnesia was first described as a constituent of urinary calculi by Dr Wollaston. It rarely exists quite alone, because the same state of the urine which leads to the formation of this species, favours the deposition of phosphate of lime; but it is frequently the prevailing ingredient. It often appears in the form of minute sparkling crystals, diffused over the surface or between the interstices of other calculous laminæ.

Calculi, in which this salt prevails, are generally white, and less compact than the foregoing species. When reduced to powder they are dissolved by cold acetic acid, and still more easily by the stronger acids, the salt being thrown down unchanged by ammonia. Digested in pure potassa it emits an ammoniacal odour, but it is not dissolved. Before the blowpipe, a smell of ammonia is given out, it diminishes in size, and melts into a white pearl with rather more facility than the phosphate of lime.

4. The fusible calculus, the nature of which was first determined by Dr Wollaston, is a mixture of the two preceding species. It is commonly of a white colour, and its fracture is usually ragged and uneven. It is more friable than any of the other kinds of calculi, separates easily into layers, and leaves a white dust on the fingers. These concretions are very common, and sometimes attain a large size.

The fusible calculus is characterized by the facility with which it melts into a pearly globule, which is sometimes quite transparent. When reduced to powder, and put into cold acetic acid, the phosphate of ammonia and magnesia is dissolved, and the phosphate of lime, almost the whole of which is left, dissolves readily in muriatic acid.

5. The mulberry calculus, so named from its resemblance to the



fruit of the mulberry, was first proved to consist of the oxalate of lime by Dr Wollaston. This concretion is sufficiently characterized by its dark-coloured tuberculated surface; but it may also be distinguished chemically by the following properties. Heated before the blowpipe, the oxalic acid is decomposed, and pure lime remains, which gives a strong brown stain to moistened turmeric paper. It is insoluble in the alkalies, but by digestion in carbonate of potassa it is decomposed, and the insoluble carbonate of lime is left. When reduced to powder and digested in muriatic or nitric acids, a perfect solution is effected. It is not dissolved by the acetic acid, a circumstance which distinguishes it from the ammoniaco-magnesian phosphate; and it is distinguished from the phosphate of lime by being insoluble in phosphoric acid.

6. The cystic oxide was described by its discoverer Dr Wollaston in the Philosophical Transactions for 1810. This concretion is not laminated, but appears as one uniform mass, confusedly crystallized through its whole substance, having somewhat the appearance of the ammoniaco-magnesian phosphate, though more compact. Before the blowpipe it emits a peculiarly fetid smell, quite distinct from that of uric acid, and is consumed. It is characterized by the great variety of reagents in which it is soluble. It is dissolved abundantly by the muriatic, nitric, sulphuric, and oxalic acids; by potassa, soda, ammonia, and lime water; and even by the neutral carbonates of soda and potassa. It is insoluble in water, alcohol, bi-carbonate of ammonia, and in the tartaric, citric, and acetic acids.

From the similarity which this substance bears to certain oxides in uniting both with acids and alkalies, Dr Wollaston termed it an oxide, and gave it the name of *cystic*, on the supposition of its being peculiar to the bladder. Dr Marcet, however, has found it in the kidney.

The cystic oxide is a rare species of calculus. In this country seven specimens only have been found;—two by Dr Wollaston, two by Dr Henry, and three by Dr Marcet. Professor Stromeyer has met with two instances of it in one family, and in one of the cases the cystic oxide was also detected in the urine. M. Lassaigne has likewise found it in a stone taken from the bladder of a dog. From the analysis of this chemist, 100 parts of cystic oxide are composed of carbon 36.2, hydrogen 12.8, oxygen 17, and nitrogen 34.

It is remarkable that the cystic oxide is never accompanied with the matter of any other concretion; whereas the other species are frequently met with in the same stone. They are sometimes so intimately mixed that they can be separated from one another only by chemical analysis, forming what is called a *compound calculus*; but more frequently the concretion consists of two or more different species arranged in distinct alternate layers. This is termed the *alternating calculus*.

Besides the calculi just mentioned, three other species have been noticed. Two of these were described by Dr Marcet under the names of *xanthic oxide* and *fibrinous calculus*, both of which are exceedingly rare. The xanthic oxide is of a reddish or yellow colour, is soluble both in acids and alkalies, and its solution in nitric acid, when evaporated, assumes a bright lemon-yellow tint, a property to which it owes its name, and by which it is characterized: (*ξανθος* yellow.) The fibrinous calculus derives its name from fibrin, to which its properties are closely analogous. The third species consists chiefly of the carbonate of lime, and is likewise of rare occurrence.



From the solubility of urinary concretions in chemical menstrua, hopes were once entertained that reagents might be introduced into the urine through the medium of the blood, or be at once injected into the bladder, so as to dissolve urinary calculi, and thus supersede the necessity of a painful operation which is not void of danger. It has been found, however, that, for this purpose, it would be necessary to employ acid or alkaline solutions of greater strength than could safely be introduced into the bladder, and consequently all attempts of the kind have been abandoned. The last suggestion of this nature was made by Messrs Prevost and Dumas, who propose to disunite the elements of calculi by means of galvanism. This agent, however, though it may produce this effect out of the body, will scarcely, I conceive, be found admissible in practice.

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## SECTION VI.

### ON THE SOLID PARTS OF ANIMALS.

#### *Bones, Horn, Membranes, Tendons, Ligaments, Muscle, &c.*

Bones consist of earthy salts and animal matter intimately blended, the former of which are designed for giving solidity and hardness, and the latter for agglutinating the earthy particles. The animal substances are chiefly cartilage, gelatine, and a peculiar fatty matter called marrow. On reducing bones to powder, and digesting them in water, the fat rises and swims upon its surface, while the gelatine is dissolved. By digesting bones in dilute muriatic acid, both the gelatine and earthy salts are dissolved, and the pure cartilage is left, which is flexible, but retains the original figure of the bone. The cartilage of bones is formed before the earthy matter, and constitutes the nidus in which the latter is deposited. In its chemical properties it is very analogous to coagulated albumen.

When bones are heated in close vessels, a large quantity of the carbonate of ammonia, some fetid empyreumatic oil, and the usual inflammable gases pass over into the recipient; while a mixture of charcoal and earthy matter, called animal charcoal, remains in the retort. If, on the contrary, they are heated to redness in an open fire, the charcoal is consumed, and a pure white friable earth is the sole residue.

According to the analysis of Berzelius, 100 parts of dry human bones consist of animal matters 33.3, phosphate of lime 51.04, carbonate of lime 11.30, fluat of lime 2, phosphate of magnesia 1.16, and soda, muriate of soda, and water 1.2. Mr Hatchett found, also, a small quantity of sulphate of lime; and Fourcroy and Vauquelin discovered traces of alumina, silica, and the oxides of iron and manganese.

Teeth are composed of the same materials as bone; but the enamel dissolves completely in dilute nitric acid, and therefore is free from cartilage. From the analysis of Mr Pepys, the enamel contains 78 per cent. of the phosphate, and 6 of the carbonate of lime, the residue

being probably gelatine. The composition of ivory is similar to that of the bony matter of teeth in general.

The shells of eggs and the covering of crustaceous animals, such as lobsters, crabs, and the starfish, consist of the carbonate and a little phosphate of lime, and animal matter. The shells of oysters, muscles, and other molluscos animals consist almost entirely of carbonate of lime and animal matter, and the composition of pearl and mother of pearl is similar.

Horn differs from bone in containing only a trace of earth. It consists chiefly of gelatine and a cartilaginous substance like coagulated albumen. The composition of the nails and hoofs of animals is similar to that of horn; and the cuticle belongs to the same class of substances.

Tendons appear to be composed almost entirely of gelatine; for they are soluble in boiling water, and the solution yields an abundant jelly on cooling. The composition of the true skin is nearly the same as that of tendons. Membranes and ligaments are composed chiefly of gelatine, but they also contain some substance which is insoluble in water, and is similar to coagulated albumen.

According to the analysis of Vauquelin, the principal ingredient of hair is a peculiar animal substance, insoluble in water at 212° F., but which may be dissolved in that liquid by means of Papin's Digester, and is soluble in a solution of potassa. Besides this substance, hair contains oil, sulphur, silica, iron, manganese, and the carbonate and phosphate of lime. The colour of the hair depends on that of its oil; and the effect of metallic solutions, such as the nitrate of silver, in staining the hair, is owing to the presence of sulphur.

The composition of wool and feathers appears analogous to that of hair. The quill part of the feather was found by Mr Hatchett to consist of coagulated albumen.

Silk is covered with a peculiar varnish which is soluble in boiling water and in alkaline solutions, and amounts to about 23 per cent. of the raw material. By digestion in alcohol it is also deprived of a portion of wax. The remaining fibrous structure has been examined in a very imperfect manner. By the action of nitric acid it is converted into a yellow crystalline substance of a bitter taste.

The flesh of animals, or *muscle*, consists essentially of fibrin; but, independently of this principle, it contains several other ingredients, such as albumen, gelatine, a peculiar extractive matter called *osmazome*, fat, and salts, substances which are chiefly derived from the blood, vessels, and cellular membrane dispersed through the muscles. On macerating flesh, cut into small fragments, in successive portions of cold water, the albumen, osmazome, and salts are dissolved; and on boiling the solution, the albumen is coagulated. From the remaining liquid the osmazome may be procured in a separate state by evaporating to the consistence of an extract, and treating it with cold alcohol. By the action of boiling water, the gelatine of the muscle is dissolved, the fat melts and rises to the surface of the water, and pure fibrin remains.

The characteristic odour and taste of soup is owing to the osmazome. This substance is of a yellowish-brown colour, and is distinguished from the other animal principles by solubility in water and alcohol, whether cold or at a boiling temperature, and by not forming a jelly when its solution is concentrated by evaporation. Like gelatine and albumen it yields a precipitate with the infusion of nut-galls.

The substance of the brain, nerves, and spinal marrow differs from that of all other animal textures. The most elaborate analysis of cerebral matter is by Vauquelin, who found that 100 parts of it consist of water 80, albumen 7, white fatty matter 4.53, red fatty matter 0.70, osmazome 1.12, phosphorus 1.5, and acids, salts, and sulphur 5.15. (*Annals of Phil.* vol. i.) The presence of albumen accounts for the partial solubility of the brain in cold water, and for the solution being coagulated by heat, acids, alcohol, and by the metallic salts which coagulate other albuminous fluids. By acting upon cerebral matter with boiling alcohol, the fatty principles and osmazome are dissolved, and the solution in cooling deposits the white fatty matter in the form of crystalline plates. On expelling the alcohol by evaporation, and treating the residue with cold alcohol, the osmazome is taken up, and a fixed oil remains of a reddish-brown colour, and an odour like that of the brain itself, though much stronger. These two species of fat differ little from each other; and both yield phosphoric acid when deflagrated with nitre.

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## SECTION VII.

### *ON PUTREFACTION.*

When dead animal matter is exposed to air, moisture, and a moderate temperature, it speedily runs into putrefaction, during which every trace of its original texture disappears, and products of a very offensive nature are generated. The presence of air, by affording oxygen, accelerates the change; but the conditions which may be regarded as essential to it, are moisture and a certain temperature, causes which operate in the same manner as in the putrefaction of vegetable matter. The most favourable temperature is from 60° to 80° or 90° Fahr. Below 50° the process takes place tardily, and at 32° it is wholly arrested;—a fact, which is clearly evinced by the circumstance that the bodies of animals, which have been buried in snow or ice, are found unchanged after a long series of years. The necessity of a certain degree of moisture is shown by the facility with which the most perishable substances may be preserved when quite dry. The preservation of smoked meat is chiefly owing to this cause; and, for a like reason, animals buried in the dry sand of Arabia and Egypt have remained for years without change.

For reasons formerly mentioned, animal matters commonly undergo putrefaction more readily than those which are derived from the vegetable kingdom; (page 347) but they are not all equally disposed to putrefy. The acid and fatty principles are less liable to this change than urea, fibrin, and other analogous substances. The chief products to which their dissolution gives rise are water, ammonia, carbonic acid, and sulphuretted, phosphuretted, and carburetted hydrogen gases.

## PART IV.

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### ANALYTICAL CHEMISTRY.

**T**O enter into a detailed account of experimental and analytical chemistry, is altogether inconsistent with the design and limits of the present work. My sole object in this department is to give a few concise directions for conducting some of the more common analytical processes; and in order to render them more generally useful, I shall give examples of the analysis of mixed gases, of minerals, and of mineral waters.

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### SECTION I.

#### ANALYSIS OF MIXED GASES.

*Analysis of air or of gaseous mixtures containing oxygen.*—Of the various processes by which oxygen gas may be withdrawn from gaseous mixtures, and its quantity determined, none are so convenient and precise as the method by means of hydrogen gas. In performing this analysis, a portion of atmospheric air is carefully measured in a graduated tube, and mixed with a quantity of hydrogen which is rather more than sufficient for uniting with all the oxygen present. The mixture is then introduced into a strong glass tube called Volta's Eudiometer, and is inflamed by the electric spark, the aperture of the tube being closed by the thumb at the moment of detonation. The total diminution in volume, divided by three, indicates the quantity of oxygen originally contained in the mixture. This operation may be performed in a trough either of water or mercury.

Instead of electricity, spongy platinum may be employed for causing the union of oxygen and hydrogen gases; and, while its indications are very precise, it has the advantage of producing the effect gradually and without detonation. The most convenient mode of employing it with this intention is the following. A mixture of spongy platinum and pipe-clay, in the proportion of about three parts of the former to one of the latter, is made into a paste with water, and then rolled between the fingers into a globular form. In order to preserve the spongy texture of the platinum, a little muriate of ammonia is mixed with the paste; and when the ball has become dry, it is cautiously ignited at the flame of a spirit-lamp. The sal-ammoniac, escaping from all parts of the mass, gives it a degree of porosity which is peculiarly favourable to its action. The ball, thus prepared, should be protected from dust and be heated to redness just before being used. To insure

accuracy, the hydrogen employed should be kept over mercury for a few hours in contact with a platinum ball and a piece of caustic potash. The first deprives it of traces of oxygen which it commonly contains, and the second of moisture and sulphuretted hydrogen. The analysis must be performed in a mercurial trough. The time required for completely removing the oxygen depends on the diameter of the tube. If the mixture is contained in a very narrow tube, the diminution does not arrive at its full extent in less than twenty minutes or half an hour; while in a vessel of an inch in diameter, the effect is complete in the course of five minutes.

*Mode of determining the quantity of nitrogen in gaseous mixtures.*—As atmospheric air, which has been deprived of moisture and carbonic acid, consists of oxygen and nitrogen only, the proportion of the latter is of course known as soon as that of the former is determined. The only method, indeed, by which chemists are enabled to estimate the quantity of this gas, is by withdrawing the other gaseous substances with which it is mixed.

*Mode of determining the quantity of carbonic acid in gaseous mixtures.*—When carbonic acid is the only acid gas which is present, as happens in atmospheric air, in the ultimate analysis of organic compounds, and in most other analogous researches, the process for determining the quantity of carbonic acid is exceedingly simple; for it consists merely in absorbing that gas by lime water or a solution of caustic potash. This is easily done in the course of a few minutes in an ordinary graduated tube; or it may be effected almost instantaneously by agitating the gaseous mixture with the alkaline solution in Hope's eudiometer. This apparatus is formed of two parts; a bottle capable of containing about twenty drachms of fluid, and furnished with a well-ground stopper; and a tube of the capacity of one cubic inch, divided into 100 equal parts, and accurately fitted by grinding to the neck of the bottle. The tube, full of gas, is fixed into the bottle previously filled with lime water, and its contents are briskly agitated. The stopper is then withdrawn under water, when a portion of liquid rushes into the tube, supplying the place of the gas which has disappeared; and the process is afterwards repeated, as long as any absorption ensues.

The eudiometer of Dr Hope was originally designed for analyzing air or other similar mixtures, the bottle being filled with a solution of the hydrosulphuret of potassa or lime, or some liquid capable of absorbing oxygen. To the employment of this apparatus it has been objected, that the absorption is rendered slow by the partial vacuum which is continually taking place within it, an inconvenience particularly felt towards the close of the process, in consequence of the eudiometric liquor being diluted by the admission of water. To remedy this defect, Dr Henry has substituted a bottle of elastic gum for that of glass, by which contrivance no vacuum can occur. From the improved method of analyzing air, however, this instrument is now rarely employed in eudiometry; but it may be used with advantage for absorbing carbonic acid or similar gases, and is particularly useful for the purpose of demonstration.

*Mode of analyzing mixtures of Hydrogen and other inflammable gases.*—When hydrogen is mixed with nitrogen, air, or other similar gaseous mixtures, its quantity is easily ascertained by causing it to combine with oxygen either by means of platinum or the electric spark. If, instead of hydrogen, any other combustible substance, such as car-



bonic oxide, light carburetted hydrogen, or olefiant gas, is mixed with nitrogen, the analysis is easily effected by adding a sufficient quantity of oxygen, and detonating the mixture by electricity. The diminution in volume indicates the quantity of hydrogen contained in the gas, and from the carbonic acid, which may then be removed by an alkali, the quantity of carbon is inferred.

When olefiant gas is mixed with other inflammable gases, its quantity is easily determined by an elegant and simple process proposed by Dr Henry. (Page 196.) It consists in mixing 100 measures, or any convenient quantity of the gaseous mixture, with an equal volume of chlorine in a vessel covered with a piece of cloth or paper, so as to protect it from light; and after an interval of about ten minutes, the excess of chlorine is removed by lime water or potassa. The loss experienced by the gas to be analyzed, indicates the exact quantity of olefiant gas which it had contained.

In mixtures of hydrogen, carburetted hydrogen, and carbonic oxide, the analytic process is exceedingly difficult and complicated, and requires all the resources of the most refined chemical knowledge, and all the address of an experienced analyst. The most recent information on this subject will be found in Dr Henry's Essay in the *Philosophical Transactions* for 1824.

## SECTION II.

### *ANALYSIS OF MINERALS.*

As the very extensive nature of this department of analytical chemistry renders a selection necessary, I shall confine my remarks solely to the analysis of those earthy minerals with which the beginner usually commences his labours. The most common constituents of these compounds are silica, alumina, iron, manganese, lime, magnesia, potassa, soda, and the carbonic and sulphuric acids; and I shall, therefore, endeavour to give short directions for determining the quantity of each of these substances.

In attempting to separate two or more fixed principles from each other, the first object of the analytical chemist is to bring them into a state of solution. If they are soluble in water, this fluid is preferred to every other menstruum; but if not, an acid or any convenient solvent may be employed. In many instances, however, the substance to be analyzed resists the action even of the acids, and in that case the following method is adopted:—The compound is first crushed by means of a hammer or a steel mortar, and is afterwards reduced to an impalpable powder in a mortar of agate; it is then intimately mixed with three, four, or more times its weight of potassa, soda, baryta, or their carbonates; and, lastly, the mixture is exposed in a crucible of silver or platinum to a strong heat. During the operation, the alkali combines with one or more of the constituents of the mineral; and, consequently, its elements being disunited, it no longer resists the action of the acids.

*Analysis of Marble or Carbonate of Lime.*—This analysis is easily made by exposing a known quantity of marble for about half an hour

to a full white heat, by which means the carbonic acid gas is entirely expelled, so that by the loss in weight the quantity of each ingredient, supposing the marble to have been pure, is at once determined. In order to ascertain that the whole loss is owing to the escape of carbonic acid, the quality of this gas may be determined by a comparative analysis. Into a small flask containing muriatic acid diluted with two or three parts of water, a known quantity of marble is gradually added, the flask being inclined to one side in order to prevent the fluid from being flung out of the vessel during the effervescence. The diminution in weight experienced by the flask and its contents, indicates the quantity of carbonic acid which has been expelled.

Should the carbonate suffer a greater loss in the fire than when decomposed by an acid, it will most probably be found to contain water. This may be ascertained by heating a piece of it to redness in a glass tube, the sides of which will be bedewed with moisture, if water is present. Its quantity may be determined by causing the watery vapour to pass through a weighed tube filled with fragments of the chloride of calcium, by which the moisture is absorbed.

*Separation of Lime and Magnesia.*—The more common kinds of carbonate of lime frequently contain traces of siliceous and aluminous earths, in consequence of which they are not completely dissolved in dilute muriatic acid. A very frequent source of impurity is the carbonate of magnesia, which is often present in such quantity that it forms a peculiar compound called *magnesian limestone*. The analysis of this substance, so far as respects carbonic acid, is the same as that of marble. The separation of the two earths may be conveniently effected in the following manner. The solution of the mineral in muriatic acid is evaporated to perfect dryness in a flat dish or *capsule* of porcelain, and after redissolving the residuum, in a moderate quantity of distilled water, a solution of the oxalate of ammonia is added as long as a precipitate ensues. The oxalate of lime is then allowed to subside, collected on a filter, converted into quicklime by a white heat, and weighed; or the oxalate may be decomposed by a red heat, the carbonate resolved into the sulphate of lime by sulphuric acid, and the excess of acid expelled by a temperature of ignition. To the filtered liquid, containing the magnesia, an excess of carbonate of ammonia, and then phosphate of soda is added, when the magnesia in the form of the ammoniaco-phosphate is precipitated. Of this precipitate, heated to redness, 100 parts correspond to 40 of pure magnesia. (Murray.)

*Earthy Sulphates.*—The most abundant of the earthy sulphates is that of lime. The analysis of this compound is easily effected. By boiling it for fifteen or twenty minutes with a solution of twice its weight of the carbonate of soda, double decomposition ensues; and the carbonate of lime, after being collected on a filter and washed with hot water, is either heated to low redness to expel the water, and weighed, or at once reduced to quicklime by a white heat. Of the dry carbonate, fifty parts correspond to twenty-eight of lime. The alkaline solution is acidulated with muriatic acid, and the sulphuric acid thrown down by the muriate of baryta. From the sulphate of this earth, collected and dried at a red heat, the quantity of acid may easily be estimated.

The method of analyzing the sulphates of strontia and baryta is somewhat different. As these salts are difficult of decomposition in the moist way, the following process is adopted. The sulphate, in fine

powder, is mixed with three times its weight of the carbonate of soda, and the mixture is heated to redness in a platinum crucible for the space of half an hour. The ignited mass is then digested in hot water, and the insoluble earthy carbonate collected on a filter. The other parts of the process are the same as the foregoing.

*Mode of analyzing compounds of Silica, Alumina, and Iron.*—Minerals, thus constituted, are decomposed by an alkaline carbonate, at a red heat, in the same manner as the sulphate of baryta. The mixture is afterwards digested in dilute muriatic acid, by which means all the ingredients of the mineral, if the decomposition is complete, are dissolved. The solution is next evaporated to dryness, the heat being carefully regulated towards the close of the process, in order to prevent any of the chloride of iron, the volatility of which is considerable, from being dissipated in vapour. By this operation, the silica, though previously held in solution by the acid, is entirely deprived of its solubility; so that on digesting the dry mass in water acidulated with muriatic acid, the alumina and iron are taken up, and the silica is left in a state of purity. The siliceous earth, after subsiding, is collected on a filter, carefullyedulcorated, heated to redness, and weighed.

To the clear liquid containing iron and alumina, a considerable excess of a solution of pure potassa is added; so as not only to throw down these oxides, but to dissolve the alumina. The peroxide of iron is then collected on a filter,edulcorated carefully until the washings cease to have an alkaline reaction, and is well dried on a sand bath. Of this hydrated peroxide, forty-nine parts contain forty of the anhydrous peroxide of iron. But the most accurate mode of determining its quantity is by expelling the water by a red heat. This operation, however, should be done with care; since any adhering particles of paper, or other combustible matter, would bring the iron into the state of black oxide, a change which is known to have occurred by the iron being attracted by a magnet.

To procure the alumina, the liquid in which it is dissolved is boiled with sal-ammoniac, when the muriatic acid unites with the potassa, the volatile alkali is dissipated in vapour, and the alumina subsides. As soon as the solution is thus rendered neutral, the hydrous alumina is collected on a filter, dried by exposure to a white heat, and quickly weighed after removal from the fire.

*Separation of iron and manganese.*—A compound of these metals or their oxide may be dissolved in muriatic acid. If the iron is in a large proportion compared with the manganese, the following process may be adopted with advantage. To the cold solution, considerably diluted with water, and acidulated with muriatic acid, carbonate of soda is gradually added, and the liquid is briskly stirred with a glass rod during the effervescence, in order that it may become highly charged with carbonic acid. By neutralizing the solution in this manner, it at length attains a point at which the peroxide of iron is entirely deposited, leaving the liquid colourless; while the manganese, by aid of the free carbonic acid, is kept in solution. The iron, after subsiding, is collected on a filter, and its quantity determined in the usual manner. The filtered liquid is then boiled with an excess of the carbonate of soda; and the precipitated carbonate of manganese is collected, heated to low redness in an open crucible, by which it is converted into the brown oxide, and weighed. This method is one of some delicacy; but in skilful hands it affords a very accurate result. It may also be employed for separating iron from magnesia and lime as well as from manganese.

But if the proportion of iron is small compared with that of manganese, the best mode of separating it is by the succinate of ammonia or soda, prepared by neutralizing a solution of succinic acid with either of those alkalies. That this process should succeed, it is necessary that the iron be wholly in the state of peroxide, that the solution be exactly neutral, which may easily be insured by the cautious use of ammonia, and that the reddish-brown coloured succinate of iron be washed with cold water. Of this succinate, well dried at a temperature of  $212^{\circ}$  F., 90 parts correspond to 40 of the peroxide. From the filtered liquid the manganese may be precipitated at a boiling temperature by carbonate of soda, and its quantity determined in the way above mentioned. The benzoate may be substituted for the succinate of ammonia in the preceding process.

It may be stated as a general rule, that whenever it is intended to precipitate iron by means of the alkalies, the succinates, or benzoates, it is essential that this metal be in the maximum of oxidation. It is easily brought into this state by digestion with a little nitric acid.

*Separation of manganese from lime and magnesia.*—If the quantity of the former be proportionally small, it is precipitated as a sulphuret by the hydrosulphuret of ammonia or potassa. This sulphuret is then dissolved in muriatic acid, and the manganese thrown down as usual by means of an alkali. But if the manganese be the chief ingredient, the best method is to precipitate it at once, together with the two earths, by a fixed alkaline carbonate at a boiling temperature. The precipitate, after being exposed to a low red heat and weighed, is put into cold water acidulated with a drop or two of nitric acid, when the lime and magnesia will be slowly dissolved with effervescence. Should a trace of the manganese be likewise taken up, it may easily be thrown down by the hydrosulphuret of ammonia.

*Mode of analyzing an earthy mineral containing silica, iron, alumina, manganese, lime, and magnesia.*—The mineral, reduced to a fine powder, is ignited with three or four times its weight of the carbonate of potassa or soda, the mass is taken up in dilute muriatic acid, and the silica separated in the way already described. To the solution, thus freed from silica and duly acidulated, carbonate of soda is gradually added, so as to charge the liquid with carbonic acid, as in the analysis of iron and manganese. In this manner the iron and alumina are alone precipitated, substances which may be separated from each other by means of pure potassa. (Page 460.) The manganese, lime, and magnesia, may be determined by the processes already described.

*Analysis of minerals containing a fixed alkali.*—When the object is to determine the quantity of fixed alkali, such as potassa or soda, it is necessary to abstain from the employment of these reagents in the analysis itself; and the beginner will do well to devote his attention to the alkaline ingredients only. On this supposition, he will proceed in the following manner. The mineral is reduced to a very fine powder, mixed intimately with six times its weight of the artificial carbonate of baryta, and exposed for an hour to a white heat. The ignited mass is dissolved in dilute muriatic acid, and the solution evaporated to perfect dryness. The soluble parts are taken up in hot water; an excess of the carbonate of ammonia is added; and the insoluble matters, consisting of silica, carbonate of baryta, and all the constituents of the mineral, excepting the fixed alkali, are collected on a filter.



The clear solution is evaporated to dryness in a porcelain capsule, and the dry mass is heated to redness in a crucible of platinum, in order to expel the salts of ammonia. The residue is the chloride of potassium or sodium.

In this analysis, it generally happens that traces of manganese, and sometimes of iron, escape precipitation in the first part of the process; and, in that case, they should be thrown down by the hydrosulphuret of ammonia. If neither lime nor magnesia is present, the alumina, iron, and manganese, may be separated by pure ammonia, and the baryta subsequently removed by the carbonate of that alkali. By this method the carbonate of baryta is recovered in a pure state, and may be reserved for another analysis. The baryta may also be thrown down as a sulphate by sulphuric acid, in which case, the soda or potassa is procured in combination with that acid.

The analysis is attended with considerable inconvenience, when magnesia happens to be present; because this earth is not completely precipitated either by ammonia or its carbonate; and, therefore, some of it remains with the fixed alkali. The best mode with which I am acquainted for effecting its separation, is the following. The carbonate of ammonia is first added, and the phosphoric acid is dropped into the liquid, until all the magnesia is thrown down in the form of the ammoniaco-magnesian phosphate. The excess of phosphoric acid is afterwards removed by the acetate of lead, and that of lead by sulphuretted hydrogen. The acetate of the alkali is then brought to dryness, ignited, and by the addition of sulphate of ammonia is converted into a sulphate.

In the preceding account, several operations have been alluded to, which, from their importance, deserve more particular mention. The process of filtering, for example, is one on which the success of analyses materially depends. Filtration is effected by means of a glass funnel, into which a filter, made of white bibulous paper, is inserted. For researches of delicacy, the filter, before being used, is macerated for a day or two in water acidulated with nitric acid, in order to dissolve lime and other substances contained in common paper, and it is afterwards washed with hot water till every trace of acid is removed. It is next dried at  $212^{\circ}$ , or any fixed temperature insufficient to decompose it, and then carefully weighed, the weight being marked upon it with a pencil. As dry paper absorbs hygrometric moisture rapidly from the atmosphere, the filter, while being weighed, should be inclosed in a light box made for the purpose. When a precipitate is collected on a filter, it is washed with pure water until every trace of the original liquid is removed. It is subsequently dried and weighed as before, and the weight of the paper subtracted from the combined weight of the filter and precipitate. The trouble of weighing the filter may sometimes be dispensed with. Some substances, such as silica, alumina, and lime, which are not decomposed when heated with combustible matter, may be put into a crucible while yet contained in the filter, the paper being set on fire before it is placed in the furnace. In these instances, the ash from the paper, the average weight of which is determined by previous experiments, must be subtracted from the weight of the heated mass.

The tests commonly employed in ascertaining the acidity or alkalinity of liquids are litmus and turmeric paper. The former is made by digesting litmus, reduced to a fine powder, in a small quantity of water, and painting with it white paper which is free from alum. The



turmeric paper is made in a similar manner ; but the most convenient test of alkalinity is litmus paper reddened by a dilute acid.

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### SECTION III.

#### ANALYSIS OF MINERAL WATERS.

Rain water collected in clean vessels in the country, or freshly fallen snow when melted, affords the purest kind of water which can be procured without having recourse to distillation. The water obtained from these sources, however, is not absolutely pure, but contains a portion of carbonic acid and air, absorbed from the atmosphere. It is remarkable that this air is very rich in oxygen. That procured from snow-water by boiling, was found by Gay-Lussac and Humboldt to contain 34.8 and that from rain water 32 per cent. of oxygen gas. From the powerfully solvent properties of water, this fluid no sooner reaches the ground and percolates through the soil, than it dissolves some of the substances which it meets with in its passage. Under common circumstances, it takes up so small a quantity of foreign matter that its sensible properties are not materially affected, and in this state it gives rise to *spring, well, and river* water. Sometimes, on the contrary, it becomes so strongly impregnated with saline and other substances, that it acquires a peculiar flavour, and is thus rendered unfit for domestic uses. It is then known by the name of *mineral waters*.

The composition of spring water is dependent on the nature of the soil through which it flows. If it has filtered through primitive strata, such as quartz rock, granite, and the like, it is in general very pure; but if it meets with limestone or gypsum in its passage, a portion of these salts is dissolved, and communicates the property called *hardness*. Hard water is characterized by decomposing soap, the lime of the former yielding an insoluble compound with the oil of the latter. If this defect is owing to the presence of the carbonate of lime, it is easily remedied by boiling, when free carbonic acid is expelled, and the insoluble carbonate of lime subsides. If sulphate of lime is present, the addition of a little carbonate of soda, by precipitating the lime, converts the hard into soft water. Besides these ingredients, the muriates of lime and soda are frequently contained in spring water.

Spring water, in consequence of its saline impregnation, is frequently unfit for chemical purposes, and on these occasions distilled water is employed. Distillation may be performed on a small scale by means of a retort, in the body of which water is made to boil, while the condensed vapour is received in a glass flask, called a *recipient*, which is adapted to its beak or open extremity. This process is more conveniently conducted, however, by means of a still.

The different kinds of mineral water may be conveniently arranged for the purpose of description in the four divisions of carbonated, chalybeate, sulphurous, and saline springs.

The carbonated springs, of which those of Seltzer, Spa, Pyrmont,

and Carlsbad are the most celebrated, are distinguished by containing a considerable quantity of free carbonic acid, owing to the escape of which they sparkle when poured from one vessel into another. They communicate a red tint to litmus paper before, but not after being boiled, and the redness disappears on exposure to the air. Mixed with a sufficient quantity of lime water, they become turbid from the deposition of carbonate of lime. They frequently contain the carbonate of lime, magnesia, and iron, in consequence of the facility with which these salts are dissolved by water charged with carbonic acid.

The best mode of determining the quantity of carbonic acid is by heating a portion of the water in a flask, and receiving the carbonic acid by means of a bent tube, in a graduated jar filled with mercury.

The chalybeate waters are characterized by a strong styptic, inky taste, and by striking a black colour with the infusion of gallnuts. The iron is sometimes combined with the muriatic or sulphuric acid; but most frequently it is in the form of a carbonate of the protoxide, held in solution by free carbonic acid. On exposure to the air, the protoxide is oxidized, and the hydrated peroxide subsides, causing the ochreous deposit, so commonly observed in the vicinity of chalybeate springs.

To ascertain the quantity of iron contained in a mineral water, a known weight of it is concentrated by evaporation, and the iron brought to the state of peroxide by means of nitric acid. The peroxide is then precipitated by an alkali and weighed; and if lime and magnesia are present, it may be separated from those earths by the process described in the last section.

Chalybeate waters are by no means uncommon; but the most noted in Britain are those of Tunbridge, Cheltenham, and Brighton. The Bath water also contains a small quantity of iron.

The sulphurous waters, of which the springs of Aix la Chapelle, Harrogate, and Moffat afford examples, contain sulphuretted hydrogen, and are easily recognised by their odour, and by causing a brown precipitate with a salt of lead or silver. The gas is readily expelled by boiling, and its quantity may be inferred by transmitting it through a solution of the acetate of lead, and weighing the sulphuret which is generated.

Those mineral springs are called saline which do not belong to either of the preceding divisions. The salts which are most frequently contained in these waters, are the sulphates, muriates, and carbonates of lime, magnesia, and soda. Potassa sometimes exists in them, and Berzelius has found lithia in the spring at Carlsbad. It has lately been discovered that the presence of hydriodic acid in small quantity is not unfrequent. As examples of saline water may be enumerated the springs of Epsom, Cheltenham, Bath, Bristol, Barèges, Buxton, Pitscaithly, and Toeplitz.

The first object in examining a saline spring is to determine the nature of its ingredients. Muriatic acid is detected by the nitrate of silver, and the sulphuric acid by muriate of baryta; and if an alkaline carbonate be present, the precipitate occasioned by either of these tests will contain a carbonate of silver or baryta. The presence of lime and magnesia may be discovered, the former by the oxalate of lime, and the latter by carbonate of ammonia and phosphoric acid. Potassa is known by the action of the muriate of platinum. (Page

238.) To detect soda, the water should be evaporated to dryness, the deliquescent salts removed by alcohol, and the matter insoluble in that menstruum taken up by a small quantity of water, and be allowed to crystallize by spontaneous evaporation. The salt of soda may then be recognised by the rich yellow colour which it communicates to flame. (Page 240.) If the presence of hydriodic acid is suspected, the solution is brought to dryness, the soluble parts dissolved in two or three drachms of a cold solution of starch, and strong sulphuric acid gradually added. (Page 182.)

Having thus ascertained the nature of the saline ingredients, their quantity may be determined by evaporating a pint of water to dryness, heating to low redness, and weighing the residue. In order to make an exact analysis, a given quantity of the mineral water is concentrated in an evaporating basin as far as can be done without causing either precipitation or crystallization, and the residual liquid is divided into two equal parts. From one portion the sulphuric and carbonic acids are thrown down by the nitrate of baryta, and after collecting the precipitate on a filter, the muriatic acid is precipitated by the nitrate of silver. The mixed sulphate and carbonate is exposed to a low red heat, and weighed; and the latter is then dissolved by dilute muriatic acid, and its quantity determined by weighing the sulphate. The chloride of silver, of which 146 parts correspond to 37 of muriatic acid, is fused in a platinum spoon or crucible, in order to render it quite free from moisture. To the other half of the concentrated mineral water, oxalate of lime is added for the purpose of precipitating the lime; and the magnesia is afterwards thrown down as the ammoniaco-phosphate, by means of the carbonate of ammonia and phosphoric acid. Having thus determined the weight of each of the fixed ingredients, excepting the soda, the loss of course gives the quantity of that alkali; or it may be procured in a separate state by the process described in the foregoing section. (Page 462.)

The individual constituent of the water being known, it remains to determine the state in which they were originally combined. In a mineral water containing sulphuric and muriatic acids, lime, and soda, it is obvious that three cases are possible. The liquid may contain sulphate of lime and muriate of soda, muriate of lime and sulphate of soda, or each acid may be distributed between both the bases. It was at one time supposed that the lime must be in combination with sulphuric acid, because the sulphate of that earth is left when the water is evaporated to dryness. This, however, by no means follows. In whatever state the lime may exist in the original spring, gypsum will be generated as soon as the concentration reaches that degree at which sulphate of lime cannot be held in solution. The late Dr Murray\*, who treated this question with much sagacity, observes that some mineral waters, which contain the four principles above mentioned, possess higher medicinal virtues than can be justly ascribed to the presence of sulphate of lime and muriate of soda. He advances the opinion that alkaline bases are united in mineral waters with those acids with which they form the most soluble compounds, and that the insoluble salts obtained by evaporation are merely products. He therefore proposes to arrange the substances determined by analysis according to this supposition. To this practice there is no objection; but it is

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\* Philosophical Transactions of Edinburgh, vol. vii.

probable that each acid is rather distributed between several bases than combined exclusively with one of them.

Sea water may be regarded as one of the saline mineral waters. Its taste is disagreeably bitter and saline, and its fixed constituents amount to about three per cent. Its specific gravity varies from 1.0269 to 1.0285; and it freezes at about 28.5° F. According to the analysis of Dr Murray, 10,000 parts of water from the Firth of Forth contain 220.01 parts of common salt, 33.16 of sulphate of soda, 42.08 of muriate of magnesia, and 7.84 of muriate of lime. Dr Wollaston has detected potassa in sea water, and it likewise contains small quantities of the hydriodic and hydro-bromic acids.

The water of the Dead Sea has a far stronger saline impregnation than sea water, containing one-fourth of its weight of solid matter. It has a peculiarly bitter, saline, and pungent taste, and its specific gravity is 1.211. According to the analysis of Dr Marcet, 100 parts of it are composed of muriate of magnesia 10.246, muriate of soda 10.36, muriate of lime 3.92, and sulphate of lime 0.054. In the river Jordan, which flows into the Dead Sea, Dr Marcet discovered the same principles as in the lake itself.

## ADDENDUM.

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### BROMINE.

THE only discovery of importance which has occurred in chemical science during the printing of this work is that of a new substance, supposed to be simple, discovered in sea water by M. Balard of Montpellier. The name first applied to it by its discoverer is *muride*; but it has since been changed to *brome*, a word derived from the Greek *βραμος*, (*graveolentia*) signifying a strong or rank odour. This appellation, for reasons which will soon be apparent, may in the English language be properly converted into that of *bromine*.

The reader will find the original essay of M. Balard in the *Annales de Chimie et de Physique* for August 1826; but the following is an abstract of the memoir published in the *Edinburgh Journal of Science*. I may add that I have confirmed several of the principal statements of M. Balard by my own observation.

At common temperatures bromine is a liquid, the colour of which is blackish-red when viewed in mass and by reflected light, but appears hyacinth-red when a thin stratum is interposed between the light and the observer. Its odour, which somewhat resembles that of chlorine, is very disagreeable; and its taste powerful. It acts with energy on organic matters, such as wood or cork, and corrodes the animal texture; but if applied to the skin for a short time only, it communicates a yellow stain, which is less intense than that produced by iodine, and soon disappears. It is highly destructive to animals, one drop of it placed on the beak of a bird having proved fatal. Its specific gravity is about 3. Its volatility is very considerable; for at common temperatures it emits red-coloured vapours, which are very similar in appearance to those of nitrous acid, and at 116.5° F. it enters into ebullition. It retains its liquid form at the temperature of zero of Fahrenheit's thermometer.

Bromine is a non-conductor of electricity, and undergoes no chemical change from the agency of the imponderables. It was transmitted through a red-hot glass tube, and exposed to the action of a Voltaic pile, sufficiently powerful for disuniting the elements of water, without evincing the least trace of decomposition. It supports combustion in a very feeble manner:—a lighted taper immersed in the vapour of bromine is soon extinguished; but before going out, it burns a few seconds with a flame which is green at its base and red at its upper part, as in an atmosphere of chlorine.

Bromine is soluble in water, in alcohol, and particularly in ether. It does not redden litmus paper, but bleaches it rapidly like chlorine; and it likewise discharges the blue colour from a solution of indigo.

From these points of close resemblance between bromine and



chlorine, M. Balard was led to examine its relations with hydrogen. No chemical action takes place between the vapour of bromine and hydrogen gas at common temperatures, not even by the agency of the direct solar rays ; but on introducing a lighted candle or a piece of red-hot iron into the mixture, combination ensues in the vicinity of the heated body, though without extending to the whole mixture, and without explosion. The union is readily effected by the action of bromine on some of the gaseous compounds of hydrogen. Thus on mixing the vapour of bromine with hydriodic acid, sulphuretted hydrogen, or phosphuretted hydrogen gas, decomposition follows, and a colourless gas, possessed of acid properties, is generated. To this gas the name of hydro-bromic acid is applied. The hydro-bromic acid gas may be conveniently procured for experimental purposes by a process similar to that for forming hydriodic acid. A mixture of bromine and phosphorus, slightly moistened, yields a large quantity of pure hydro-bromic acid gas, which may be collected over mercury.

The hydro-bromic acid gas is colourless, has an acid taste, and a pungent odour. It irritates the glottis powerfully, so as to excite cough, and when mixed with moist air, yields white vapours, which are denser than those occasioned under the same circumstances by muriatic acid gas. It undergoes no decomposition when transmitted through a red-hot tube, either alone or mixed with oxygen. It is not affected by iodine ; but chlorine decomposes it instantly, with production of muriatic acid gas, and deposition of bromine. It may be preserved without change over mercury ; but potassium and tin decompose it with facility, the first at common temperatures, and the last by the aid of heat.

The hydro-bromic acid is very soluble in water. The aqueous solution may be made by treating bromine with sulphuretted hydrogen dissolved in water, or still better, by transmitting a current of hydro-bromic acid gas through pure water. The liquid becomes hot during the condensation, acquires great density, increases in volume, and emits white fumes when exposed to the air. This acid solution is colourless when pure, but possesses the property of dissolving a large quantity of bromine, and then receives the tint of that substance.

Chlorine decomposes the solution of hydro-bromic acid in an instant. Nitric acid likewise acts upon it, though less suddenly, occasioning the disengagement of bromine, and probably the formation of water and nitrous acid. The nitro-hydro-bromic acid is analogous to *aqua regia*, and possesses the property of dissolving gold.

The elements of sulphuric and hydro-bromic acid react on each other in a slight degree ; and hence on decomposing the hydro-bromate of potassa by sulphuric acid, the hydro-bromic is generally mixed with a little sulphurous acid gas.

The metallic oxides, as might be expected, do not act in a uniform manner on the hydro-bromic acid. The alkalis, earths, the oxides of iron, and the peroxides of copper and mercury, form compounds which may be regarded as hydro-bromates ; whereas the oxide of silver, and the protoxide of lead, give rise to double decomposition, in consequence of which water and a metallic bromuret result.

The composition of hydro-bromic acid gas is easily inferred from the two following facts. 1. On decomposing hydro-bromic acid by potassium, a quantity of hydrogen remains precisely equal to half the volume of the gas employed ; and 2, when hydriodic acid gas is decomposed by bromine, the resulting hydro-bromic acid occupies the

very same space as the gas which is decomposed. It is hence apparent that the hydro-bromic is analogous to hydriodic and muriatic acid gases; or, in other words, that 100 measures of hydro-bromic acid gas contain fifty measures of the vapour of bromine, and fifty of hydrogen.

Since bromine decomposes the hydriodic, and chlorine the hydro-bromic acid, it is obvious that bromine, in relation to hydrogen, is intermediate between chlorine and iodine, its affinity for that substance being weaker than the first, and stronger than the second. The affinity of bromine and oxygen for hydrogen appears nearly similar; for while oxygen cannot detach hydrogen from bromine, bromine does not decompose watery vapour.

The action of bromine on the metals presents the closest resemblance to that which chlorine exerts on the same substances. Antimony and tin take fire by contact with bromine; and its union with potassium is attended with such intense disengagement of heat as to cause a vivid flash of light, and to burst the vessel in which the experiment is performed. M. Balard is of opinion, that the soluble metallic bromurets are converted, like the similar compounds of chlorine and iodine, into neutral hydro-bromates; and reciprocally, that the hydro-bromates are frequently converted into bromurets in passing into the solid state. All the bromurets are decomposed by chlorine with evolution of bromine; and the hydro-bromates are not only attacked by chlorine, but by all substances, such as the chloric or nitric acids, which have a strong tendency to deprive other bodies of hydrogen.

The bromuret of potassium, which may be obtained in cubic crystals from the hydro-bromate of potassa by evaporation, was found by M. Balard to consist of

Bromine	.	.	.	65.56
Potassium	.	.	.	34.44

And hence, supposing it to contain one atom of each element, the weight of an atom of bromine will be represented by 9.326, that of oxygen being regarded as unity.

Ammoniacal gas unites with its own volume of hydro-bromic acid gas, forming a white, solid, volatile salt, which is soluble in water, and crystallizes in long prisms by evaporation.

The hydro-bromate of baryta is very soluble in water, and is also dissolved by alcohol. It forms opaque mammillated crystals, which have no resemblance to the transparent scales of the muriate of barytes.

The hydro-bromate of magnesia is deliquescent and uncrystallizable, and, like the muriate of that base, is decomposed by an elevated temperature.

On mixing a soluble hydro-bromate with the nitrates of lead, silver, and the protoxide of mercury, white precipitates are obtained, which are very similar to the chlorides of those metals, and which appear to be metallic bromurets. By the action of bromine on metallic mercury, a compound results which yields the peroxide of mercury when decomposed by alkalis, and must therefore be a bi-bromuret. It may be sublimed by heat, is soluble in water, alcohol, and ether, particularly in the last, and presents a close analogy to corrosive sublimate. It is distinguished from that substance, however, by yielding the red vapours of bromine when treated by the nitric, and still better by the sulphuric acid.

The bromuret of silver has the same curdy appearance as the chloride, becomes black by exposure to light, is soluble in ammonia, and insoluble

ble in nitric acid, which does not decompose it even at a boiling temperature. Boiling sulphuric acid, on the contrary, detaches some vapours of bromine. The bromuret of silver is decomposed by hydrogen in a nascent state, and was found by M. Balard to consist of

Silver,	.	.	589
Bromine,	.	.	411
			<hr/>
			1000

The atomic weight of bromine, estimated from these data, is 9.429.

Bromine acts upon metallic oxides much in the same manner as chlorine. On passing the vapour of bromine over potassa, soda, baryta, or lime, a vivid incandescence ensues, oxygen is disengaged, and a metallic bromuret results. Magnesia and zirconia are not decomposed by this treatment.

When bromine acts on the solution of an alkali or alkaline earth, considerably diluted with water, the bromuret of an oxide is produced, which possesses bleaching properties, and from which acetic acid causes the disengagement of bromine. But when this substance acts upon a concentrated solution of potassa, or when solid potassa is agitated with the ethereal solution of bromine, two salts are generated, the hydro-bromate and bromate of potassa; and on evaporating the solution, the former is obtained in cubic, and the latter in acicular crystals. The bromate of potassa is separated from the hydro-bromate by being very sparingly soluble in cold water. The alkaline earths likewise cause the formation of the two acids, but magnesia does not appear to possess that property.

The bromates are analogous to the chlorates and iodates. Thus the bromate of potassa is converted by heat into the bromuret of potassium, with disengagement of pure oxygen, deslagrates when thrown on burning charcoal, and forms with sulphur a mixture which detonates by percussion. The acid of the bromates is decomposed by deoxidizing agents, such as the sulphurous acid and sulphuretted hydrogen, in the same manner as the acid of the iodates. The bromates likewise suffer decomposition from the action of hydro-bromic and muriatic acids.

The bromate of potassa does not precipitate the salts of lead; but occasions a white precipitate with the nitrate of silver, and a yellowish-white with the proto-nitrate of mercury;—characters which, if correctly observed, distinguish the bromate from the iodate and chlorate of potassa in a very satisfactory manner.

The bromic acid may be procured in a separate state by decomposing a dilute solution of the bromate of baryta with sulphuric acid. From the analysis of bromate of potassa it appears to consist of one atom of bromine and five atoms of oxygen, and is consequently similar in constitution to the iodic, chloric, and nitric acids.

Bromine unites with chlorine at common temperatures, forming a very volatile liquid of a reddish-yellow colour, penetrating odour, and exceedingly disagreeable taste. It is soluble in water, and dissolves in that liquid apparently without decomposition; for the solution bleaches litmus paper without previously reddening it, and has the characteristic odour and colour of the compound. By the action of alkalies it is resolved into muriatic and bromic acids. M. Balard has also described compounds of bromine with iodine, phosphorus, and sulphur. With olefiant gas it produces an oily fluid, denser than water, and of a mild

ethereal odour. This substance, when transmitted through a red-hot tube, suffers decomposition, charcoal being deposited, and hydro-bromic acid gas evolved. It is therefore very analogous to the hydrocarburet of chlorine.

Bromine exists in sea water in the form of hydro-bromic acid, combined, in the opinion of M. Balard, with magnesia. It is present, however, in very small quantity; and even the uncrystallizable residue, called *bittern*, left after the muriate of soda has been separated from sea water by evaporation, contains but little of it. On adding chlorine to this liquid, an orange-yellow tint appears; and on heating the solution to the boiling point, the red vapours of bromine are expelled, which may be condensed by a freezing mixture. A better process for preparing bromine is to transmit a current of chlorine gas through the *bittern*, and then to agitate a portion of ether with the liquid. The ether dissolves the whole of the bromine, from which it receives a beautiful hyacinth red tint, and, on standing, rises to the surface. When the ethereal solution is agitated with caustic potash, its colour entirely disappears, and, on evaporation, cubic crystals of the hydrobromate of potash are deposited.

M. Balard has ascertained that bromine exists in marine plants which grow on the shores of the Mediterranean Sea, and has procured it in appreciable quantity from the ashes of the sea-weeds that furnish iodine. He has likewise detected its presence in the ashes of some animals, especially in those of the *Janthina violacea*, one of the testaceous mollusca.

From the circumstance of bromine being intermediate between chlorine and iodine in some of its more important chemical relations, M. Balard at first suspected it to be some unknown compound of these bodies; but as, on further examination, he failed in obtaining the least trace of decomposition, he was induced to adopt the opinion that it is an elementary substance. The facts which have been related are greatly in favour of this view. They have not, however, as yet, been confirmed by other chemists, and therefore it would be premature to form a decided opinion on the subject. I may observe, however, that MM. Vauquelin, Thénard, and Gay-Lussac, in their report to the Parisian Academy of Sciences, speak in the most flattering terms of the memoir of M. Balard, and, though they express themselves in a very cautious manner, regard his opinion as highly probable.





## APPENDIX.

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### *TABLE of Chemical Equivalents, Atomic Weights, or Proportional Numbers, Hydrogen being taken as Unity.*

**I**N preparing the following tabular view of the atomic weights, I have chiefly consulted the table published by Dr Thomson in his *First Principles of Chemistry*, and by Mr Phillips in the new series, 10th volume, of the *Annals of Philosophy*. From the full account already given of the Laws of Combination and of the Atomic Theory, it will be superfluous to describe the uses of the table. The only explanation required on this subject, relates to the ingenious contrivance of Dr Wollaston, called the *Scale of Chemical Equivalents*. This useful instrument is a table of atomic weights, comprehending all those substances which are most frequently employed by chemists in the laboratory; and it only differs from other tabular arrangements of the same kind, in the numbers being attached to a sliding rule, which is divided according to the principle of that of Gunter. From the mathematical construction of the scale, it not only serves the same purpose as other tables of atomic weights, but in many instances supersedes the necessity of calculation. Thus, by inspecting the common table of atomic weights, we learn that 88 parts, or one atom, of the sulphate of potassa contain 40 parts of sulphuric acid and 48 of potassa; but recourse must be had to calculation when it is wished to determine the quantity of acid or alkali in any other quantity of the salt. This knowledge, on the contrary, is obtained directly by means of the scale of chemical equivalents. For example, on pushing up the slide until 100, marked upon it, is in a line with the name sulphate of potassa on the fixed part of the scale, the numbers opposite to the terms sulphuric acid and potassa, will give the precise quantity of each contained in 100 parts of the compound. In the original scale of Dr Wollaston, for a particular account of which I may refer to the *Philosophical Transactions* for 1814, oxygen is taken as the standard of comparison; but hydrogen may be selected for that purpose with equal propriety.

Acid, acetic, . . . . .	50	Acid, benzoic, . . . . .	120
c. 1 w.* . . . .	59	boracic, (b. 8 + o. 16)	24
arsenic, (a. 38 + o. 24)	62	c. 2 w. . . . .	42
arsenious, (a. 38 + o. 16)	54	carbonic, (c. 6 + o. 16)	22

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\* C means crystallized, w, water; and the numeral before w, expresses the number of atoms of water which the crystals contain.

Acid, chloric, (chl. 36 + o. 40)	76	Acid, sulphuric, dry (s. 16 + o. 24)	40
chloriodic, (chl. 72 + iod. 124)	196	liquid, (sp. gr. 1.8438.)	1 w. 49
chloro-carbonic, (chl. 36 + carb. oxide 14)	50	sulphurous (s. 16 + o. 16)	32
chlorocyanic (chl. 36 + cyan. 26)	62	tartaric,	66
chromic, (chr. 28 + o. 24)	52	c. 1 w.	75
citric,	58	titanic,	48
c. 2 w.	76	tungstic, (t. 96 + o. 24)	120
columbic,	152	uric,	72
fluoboric, (bor. a. 24 + fl. a. 10)	34	Alcohol, (olef. gas 14 + aq. vap. 9)	23
fluoric,	10	Alum, anhydrous,	262
formic,	37	c. 25 w.	487
fluosilicic, (fl. a. 10 + sil. 16)	26	Alumina,	18
gallic?	62	sulphate,	58
hydriodic, (iod. 124 + hyd. 1.)	125	Aluminum,	10
hydrocyanic, (cyan. 26 + hyd. 1)	27	Ammonia, (nit. 14 + hyd. 3)	17
hyposulphurous, (s. 16 + o. 8)	24	Antimony,	44
hyposulphuric, (s. 32 + o. 40)	72	chloride, (ant. 44 + chl. 36)	80
iodic, (iod. 124 + o. 40)	164	iodide, (ant. 44 + iod. 124)	168
malic,	70	oxide, (ant. 44 + o. 8.)	52
manganeseous?	52	deutoxide,	56
manganesic?	60	peroxide,	60
molybdous,	64	sulphuret,	60
molybdic,	72	Arsenic,	38
muriatic, (chl. 36 + hyd. 1)	37	sulphuret, (realgar)	54
nitric, dry (nit. 14 + o. 40)	54	sesquisulphuret*, (orpi-ment)	62
nitric, liquid (sp. gr. 1.5)	72	Barium	70
2 w.	72	chloride, (b. 70 + chl. 36)	106
nitrous (nit. 14 + o. 32)	46	iodide, (b. 70 + iod. 124)	194
oxalic,	36	oxide, (baryta)	78
c. 4 w.	72	peroxide?	86
perchloric, (chl. 36 + o. 56)	92	phosphuret,	82
phosphorous, (p. 12 + o. 8)	20	sulphuret,	86
phosphoric, (p. 12 + o. 16)	28	Bismuth,	72
saccholactic,	104	chloride, (b. 72 + chl. 36)	108
selenic, (sel. 40 + o. 16)	56	oxide,	80
succinic,	50	iodide, (b. 72 + iod. 124)	196
		phosphuret, (b. 72 + p. 12)	84
		sulphuret, (b. 72 + s. 16)	88
		Boron,	8
		Cadmium,	56

\* 1 Proportion of arsenic, and  $1\frac{1}{2}$  sulphur.

Cadmium, chloride, (cad. 56 + chl. 36)	92	Fluorine,	.	.	18
oxide,	64	Glucinum,	.	.	18
iodide,	144	Glucina,	.	.	26
phosphuret,	68	Gold,	.	.	200
sulphuret,	72	chloride, (g. 200 + chl. 36)	.	.	236
Calcium,	20	bichloride, (g. 200 + chl. 72)	.	.	272
chloride, (cal. 20 + chl. 36)	56	iodide, (g. 200 + iod. 124)	.	.	324
iodide,	144	oxide, (g. 200 + o. 8)	.	.	208
oxide, (lime)	28	peroxide, (g. 200 + o. 24)	.	.	224
phosphuret,	32	sulphuret, (g. 200 + s. 48)	.	.	248
sulphuret,	36	Hydrogen,	.	.	1
Carbon,	6	arseniuretted, (a. 38 + h. 1)	.	.	39
bisulphuret, (c. 6 + s. 32)	38	carburetted, (c. 6 + h. 2)	.	.	8
chloride,	42	bicarburetted, (olefiant gas) (c. 12 + h. 2.)	.	.	14
perchloride,	120	seleniuretted, (s. 40 + h. 1)	.	.	41
oxide,	14	sulphuretted, (s. 16 + h. 1)	.	.	17
phosphuret,	18	bisulphuretted, (s. 32 + h. 1)	.	.	33
Cerium,	50	Hydruret of phosphorus,	.	.	13
oxide,	58	Bi-hydruret of phosphorus,	.	.	14
peroxide,	62	Iodine,	.	.	124
Chlorine,	36	Iridium,	.	.	30
hydrocarburet, (chl. 36 + olef. gas 14)	50	Iron,	.	.	28
oxide, (chl. 36 + o. 8)	44	chloride, (i. 28 + chl. 36)	.	.	64
peroxide,	68	perchloride, (i. 28 + chl. 54)	.	.	82
Chromium,	28	iodide (i. 28 + iod. 124)	.	.	152
oxide,	36	oxide, (i. 28 + o. 8)	.	.	36
deutoxide,	44	peroxide, (i. 28 + o. 12)	.	.	40
Cobalt,	26	sulphuret, (i. 28 + s. 16)	.	.	44
chloride, (cob. 26 + chl. 36)	62	bisulphuret, (i. 28 + s. 32)	.	.	60
iodide,	150	Lead,	.	.	104
oxide,	34	chloride, (l. 104 + chl. 36)	.	.	140
peroxide,	38	oxide, (l. 104 + o. 8)	.	.	112
phosphuret,	38	deutoxide, (l. 104 + o. 12)	.	.	116
sulphuret,	42	peroxide, (l. 104 + o. 16)	.	.	120
Columbium,	144	phosphuret, (l. 104 + p. 12)	.	.	116
Copper,	64	sulphuret, (l. 104 + s. 16)	.	.	120
chloride, (cop. 64 + chl. 36)	100	Lithium,	.	.	10
bi-chloride, (c. 64 + chl. 72)	136	chloride (l. 10 + ch. 36)	.	.	46
iodide, (c. 64 + iod. 124)	188	iodide,	.	.	134
oxide, (c. 64 + o. 8)	72	oxide, (lithia)	.	.	18
peroxide, (c. 64 + o. 16)	80	sulphuret,	.	.	26
phosphuret,	76				
sulphuret,	80				
bi-sulphuret,	96				
Cyanogen, (carb. 12 + nit. 14)	26				
Cyanuret of sulphur, (cy. 26 + s. 32)	58				
Ether, (olef. gas. 28 + wat. vap. 9)	37				

Magnesium, . . . . .	12	Platinum, oxide, . . . . .	104
chloride, (m. 12 + chl. 36)	48	deutoxide, . . . . .	112
oxide (magnesia,) . . . . .	20	sulphuret, . . . . .	112
sulphuret, . . . . .	28	bisulphuret, . . . . .	128
Manganese, . . . . .	28	Potassium, . . . . .	40
chloride, (m. 28 + chl. 36)	64	chloride, (p. 40 + chl. 36)	76
oxide, (m. 28 + o. 8)	36	iodide, . . . . .	164
deutoxide, (m. 28 + o. 12)	40	oxide, (potassa) . . . . .	48
peroxide, (m. 28 + o. 16)	44	peroxide, (p. 40 + o. 24)	64
sulphuret, . . . . .	44	phosphuret, . . . . .	52
Mercury, . . . . .	200	sulphuret . . . . .	56
chloride, (calomel) (m. 200 + chl. 36)	236	Rhodium, . . . . .	44
bichloride, (corros. subl.) (m. 200 + chl. 72)	272	oxide, . . . . .	52
iodide, (m. 200 + iod. 124)	324	peroxide, . . . . .	60
biniodide, (m. 200 + iod. 248)	448	Selenium, . . . . .	40
oxide, (m. 200 + o. 8)	208	Silica, . . . . .	16
peroxide, (m. 200 + o. 16)	216	Silicium, . . . . .	8
sulphuret, . . . . .	216	Silver, . . . . .	110
bisulphuret, . . . . .	232	chloride, (s. 110 + chl. 36)	146
Molybdenum, . . . . .	48	iodide, . . . . .	234
oxide, (m. 48 + o. 8)	56	oxide, (s. 110 + o. 8)	118
deutoxide, (m. 48 + o. 16)	64	phosphuret, . . . . .	122
Molybdic acid, (m. 48 + o. 24)	72	sulphuret, . . . . .	126
Nickel, (Lassaigne) . . . . .	40	Sodium, . . . . .	24
chloride, (n. 40 + chl. 36)	76	chloride, (s. 24 + chl. 36)	60
iodide, . . . . .	164	iodide, . . . . .	148
oxide, (n. 40 + o. 8)	48	oxide, (soda) . . . . .	32
peroxide, (n. 40 + o. 16)	56	peroxide, (s. 24 + o. 12)	36
phosphuret, . . . . .	52	phosphuret, . . . . .	36
sulphuret, . . . . .	56	sulphuret, . . . . .	40
Nitrogen, . . . . .	14	Strontium, . . . . .	44
bicarburet, (cyanogen) . . . . .	26	chloride, . . . . .	80
chloride, (n. 14 + chl. 144)	158	iodide, . . . . .	140
iodide, (n. 14 + iod. 372)	386	oxide, (strontia) . . . . .	52
oxide, (n. 14 + o. 8)	22	phosphuret, . . . . .	56
deutoxide, (n. 14 + o. 16)	30	sulphuret, . . . . .	60
Oxygen, . . . . .	8	Sulphur, . . . . .	16
Palladium, . . . . .	56	chloride, (s. 16 + chl. 36)	52
oxide, . . . . .	64	iodide, (s. 16 + iod. 124)	140
Phosphorus, . . . . .	12	phosphuret, . . . . .	28
chloride, (p. 12 + chl. 36)	48	Sulphuretted hydrogen, . . . . .	17
bichloride, . . . . .	84	Bisulphuretted hydrogen, . . . . .	33
carburet, . . . . .	18	Tellurium, (Berzelius) . . . . .	32
sulphuret, . . . . .	28	chloride, . . . . .	68
Platinum, . . . . .	96	oxide, . . . . .	40
chloride, (p. 96 + chl. 36)	132	Tin, . . . . .	58
bichloride, . . . . .	168	chloride, (t. 58 + chl. 36)	94
		bichloride, . . . . .	130
		oxide, . . . . .	66
		deutoxide, . . . . .	74
		phosphuret, . . . . .	70
		sulphuret, . . . . .	74
		bisulphuret, . . . . .	90
		Titanium, . . . . .	32

Titanium, oxide, . . .	40	Arsenate of soda, . . .	94
Titanic acid, . . .	48	Binarsenate of soda, c. 5 w. . .	201
Tungsten, . . .	96	Arsenate of strontia, . . .	114
oxide, (brown), (t. 96 + o. 16) . . .	112	silver, . . .	180
Tungstic acid, (t. 96 + o. 24) . . .	120	Arsenite of lime, . . .	82
Uranium, . . .	208	potassa, . . .	102
oxide, . . .	216	Arsenite of soda, . . .	86
peroxide, . . .	224	silver, . . .	172
Water, . . .	9	Carbonate of ammonia, (carb. a. 22 + am. 17.) . . .	39
Yttrium, . . .	34	Sesquicarbonate of ammonia, (carb. a. 33. + am. 17. + w. 9.) . . .	59
Oxide, (Yttria) . . .	42	Bicarbonate of do. 1 w. . .	70
Zinc, . . .	34	Carbonate of baryta, . . .	100
chloride, . . .	70	copper, . . .	102
oxide, . . .	42	iron, (protoxide) . . .	58
phosphuret, . . .	46	lead . . .	134
sulphuret, . . .	50	lime, . . .	50
Zinconium, . . .	40	magnesia, . . .	42
Zirconia, . . .	48	manganese, . . .	58
		potassa, . . .	70

*Salts.*

Acetate of alumina, (ac. a. 50 + al. 18.) . . .	68	Bicarbonate of potassa, . . .	92
c. 1 w. . .	77	c. 1 w. . .	101
ammonia (ac. a. 50 + am. 17.) . . .	67	Carbonate of soda, . . .	54
c. 7 w. . .	130	c. 10 w. . .	144
baryta, (ac. a. 50 + b. 78.) . . .	128	Bicarbonate of soda, c. 1 w. . .	85
c. 3 w. . .	155	Carbonate of strontia, . . .	74
cadmium, (c. 2 w.) . . .	132	zinc, . . .	64
copper, (ac. a. 50 + perox. 80.) . . .	130	Chlorate of baryta, (ch. a. 76 + b. 78) . . .	154
c. 6 w. (com. verdigris,) . . .	184	lead, . . .	188
binacetate, . . .	180	mercury, . . .	284
c. 3 w. (distilled verdigris,) . . .	207	potassa, . . .	124
subacetate, (ac. a. 50 + perox. 160) . . .	210	Chromate of baryta, . . .	130
lead, . . .	162	lead, . . .	164
c. 3 w. . .	189	mercury, . . .	260
lime, . . .	78	potassa, (chr. a. 52. + p. 48) . . .	100
magnesia, . . .	70	Bichromate of potassa, . . .	152
mercury, (protoxide) c. 4 w. . .	294	Fluate of baryta, . . .	88
potassa, . . .	98	lead, . . .	122
silver, . . .	168	lime, . . .	38
strontia, c. 1 w. . .	111	Muriate of ammonia, (mur. a. 37 + am. 17.) . . .	54
zinc, . . .	92	baryta, c. 1 w. . .	124
c. 7 w. . .	155	lime, c. 6 w. . .	119
Arsenate of lead, . . .	174	magnesia, . . .	57
lime, . . .	90	strontia, c. 8 w. . .	161
magnesia, . . .	82	Nitrate of ammonia, (nit. a. 54 + am. 17) . . .	71
potassa, . . .	110	baryta, . . .	132
Binarsenate of potassa, c. 1 w. . .	181	bismuth, c. 3 w. . .	161
		lead, . . .	166
		lime, . . .	82



Nitrate of magnesia, . . .	74	Sulphate of copper, (sulph. a. 40 + perox. 80) . . .	120
mercury (protoxide,) . . .	280	Bisulphate of do. . .	160
c. 2 w. . .	102	c. 10 w. (blue vitriol,) . . .	250
potassa, . . .	172	Sulphate of iron, (protoxide) . . .	76
silver, . . .	86	c. 7 w. (green vitriol) . . .	139
soda, . . .	106	lead, . . .	152
strontia, . . .	53	lime, . . .	68
Oxalate of ammonia, (Ox. a. 36 + am. 17) . . .	71	c. 2 w. . .	86
c. 2 w. . .	114	lithia, c. 1 w. . .	67
baryta, . . .	150	magnesia, c. 7 w. . .	123
Binoxalate of baryta, . . .	70	mercury, (sulph. a. 40 + perox. 216) . . .	256
Oxalate of cobalt, . . .	64	Bisulphate of mercury, (peroxide) . . .	296
lime, . . .	84	Sulphate of potassa, . . .	88
nickel, . . .	84	Bisulphate of potassa, c. 2 w. . .	146
potassa, . . .	93	Sulphate of soda, . . .	72
c. 1 w. . .	120	c. 10 w. . .	162
Binoxalate of potassa, . . .	138	strontia, . . .	92
c. 2 w. . .	192	zinc, . . .	82
Quadroxalate of potassa, . . .	255	c. 7 w. . .	145
c. 7 w. . .	88	Sulphate of alumina and potassa, . . .	262
Oxalate of strontia, . . .	124	c. 25 w. (alum) . . .	487
Binoxalate of strontia, . . .	63	Nitrate of lead, . . .	178
Phosphate of ammonia, c. 2 w. . .	106	lime, . . .	94
baryta, . . .	140	potassa, . . .	88
lead, . . .	56	Bitartrate of potassa, . . .	180
lime, . . .	48	c. 2 w. (cream of tartar) . . .	198
magnesia, . . .	60	Tartrate of antimony and potassa, c. 3 w. (tartar emetic,) . . .	363
soda, . . .	168		
c. 12 w. . .	58		
Sulphate of alumina, . . .	66		
ammonia, c. 1 w. . .	118		
baryta, . . .			

TABLE II.

*TABLE of the Elastic Force of Aqueous Vapour at different Temperatures, expressed in inches of Mercury.*

Temp.	Force of Vapour.		Temp.	Force of Vapour.		Temp.	Force of Vapour.	
	Dalton.	Ure.		Dalton.	Ure.		Dalton.	Ure.
32° F.	0.200	0.200	72° F.	0.770		112° F.	2.68	
33	0.207		73	0.796		113	2.76	
34	0.214		74	0.823		114	2.84	
35	0.221		75	0.854	0.860	115	2.92	2.820
36	0.229		76	0.880		116	3.00	
37	0.237		77	0.910		117	3.08	
38	0.245		78	0.940		118	3.16	
39	0.254		79	0.971		119	3.25	
40	0.263	0.250	80	1.00	1.010	120	3.33	3.300
41	0.273		81	1.04		121	3.42	
42	0.283		82	1.07		122	3.50	
43	0.294		83	1.10		123	3.59	
44	0.305		84	1.14		124	3.69	
45	0.316		85	1.17	1.170	125	3.79	3.830
46	0.328		86	1.21		126	3.89	
47	0.339		87	1.24		127	4.00	
48	0.351		88	1.28		128	4.11	
49	0.363		89	1.32		129	4.22	
50	0.375	0.360	90	1.36	1.360	130	4.34	4.366
51	0.388		91	1.40		131	4.47	
52	0.401		92	1.44		132	4.60	
53	0.415		93	1.48		133	4.73	
54	0.429		94	1.53		134	4.86	
55	0.443	0.416	95	1.58	1.640	135	5.00	5.070
56	0.458		96	1.63		136	5.14	
57	0.474		97	1.68		137	5.29	
58	0.490		98	1.74		138	5.44	
59	0.507		99	1.80		139	5.59	
60	0.524	0.516	100	1.86	1.860	140	5.74	5.770
61	0.542		101	1.92		141	5.90	
62	0.560		102	1.98		142	6.05	
63	0.578		103	2.04		143	6.21	
64	0.597		104	2.11		144	6.37	
65	0.616	0.630	105	2.18	2.100	145	6.53	6.600
66	0.616		106	2.25		146	6.70	
67	0.655		107	2.32		147	6.87	
68	0.676		108	2.39		148	7.05	
69	0.698		109	2.46		149	7.23	
70	0.721	0.726	110	2.53	2.456	150	7.42	7.530
71	0.745		111	2.60		151	7.61	

TABLE II. CONTINUED.

Temp.	Force of Vapour.		Temp.	Force of Vapour.		Temp.	Force of Vapour.	
	Dalton.	Ure.		Dalton.	Ure.		Dalton.	Ure.
152° F.	7.81		198° F.	22.69		244° F.	53.03	
153	8.01		199	23.16		245	53.88	56.340
154	8.20		200	23.64	23.600	246	54.68	
155	8.40	8.500	201	24.12		247	55.54	
156	8.60		202	24.61		248	56.42	60.400
157	8.81		203	25.10		249	57.31	
158	9.02		204	25.61		250	58.21	61.900
159	9.24		205	26.13	25.900	251	59.12	63.500
160	9.46	9.600	206	26.66		252	60.05	
161	9.68		207	27.20		253	61.00	
162	9.91		208	27.74		254	61.92	66.700
163	10.15		209	28.29		255	62.85	67.250
164	10.41		210	28.84	28.880	256	63.76	
165	10.68	10.800	211	29.41		257	64.82	69.800
166	10.96		212	30.00	30.000	258	65.78	
167	11.25		213	30.60		259	66.75	
168	11.54		214	31.21		260	67.73	72.300
169	11.83		215	31.83		261	68.72	
170	12.13	12.050	216	32.46	33.400	262	69.72	75.900
171	12.43		217	33.09		263	70.73	
172	12.73		218	33.72		264	71.74	77.900
173	13.02		219	34.35		265	72.76	78.040
174	13.32		220	34.99	35.540	266	73.77	
175	13.62	13.550	221	35.63	36.700	267	74.79	81.900
176	13.92		222	36.25		268	75.80	
177	14.22		223	36.88		269	76.82	84.900
178	14.52		224	37.53		270	77.85	86.300
179	14.83		225	38.20	39.110	271	78.89	88.000
180	15.15	15.160	226	38.89	40.100	272	79.94	
181	15.50		227	39.59		273	80.98	91.200
182	15.86		228	40.30		274	82.01	
183	16.23		229	41.02		275	83.13	93.480
184	16.61		230	41.75	43.100	276	84.35	
185	17.00	16.900	231	42.49		277	85.47	97.800
186	17.40		232	43.24		278	86.50	
187	17.80		233	44.00		279	87.63	101.600
188	18.20		234	44.78	46.800	280	88.75	101.900
189	18.60		235	45.58	47.220	281	89.87	104.400
190	19.00	19.000	236	46.39		282	90.99	
191	19.42		237	47.20		283	92.11	107.700
192	19.86		238	48.02	50.300	284	93.23	
193	20.32		239	48.84		285	94.35	112.200
194	20.77		240	49.67	51.700	286	95.48	
195	21.22	21.100	241	50.50		287	96.64	114.800
196	21.68		242	51.34	53.600	288	97.80	
197	22.13		243	52.18		289	98.96	118.200

TABLE II. CONTINUED.

Temp.	Force of Vapour.		Temp.	Force of Vapour.		Temp.	Force of Vapour.	
	Dalton.	Ure.		Dalton.	Ure.		Dalton.	Ure.
290° F.	100.12	120.150	302° F.	114.15	144.300	314° F.	128.15	
291	101.28		303	115.32	147.700	315	129.29	
292	102.45	123.100	304	116.50		316	130.43	
293	103.63		305	117.68	150.560	317	131.57	
294	104.80	126.700	306	118.86	154.400	318	132.72	
295	105.97	130.400	307	120.03		319	133.86	
296	107.14		308	121.20	157.700	320	135.00	
297	108.31	133.900	309	122.37		321	136.14	
298	109.48	137.400	310	123.53	161.300	322	137.28	
299	110.64		311	124.69	164.800	323	138.42	
300	111.81	139.700	312	125.85	167.000	324	139.56	
301	112.98		313	127.00		325	140.70	

TABLE III.

*Dr Ure's Table, showing the Elastic Force of the Vapours of Alcohol, Ether, Oil of Turpentine, and Petroleum or Naphtha at different Temperatures, expressed in Inches of Mercury.*

Ether.		Alcohol sp. gr. 0.813.		Alcohol sp. gr. 0.813.		Petroleum.	
Temp.	Force of Vapour.	Temp.	Force of Vapour.	Temp.	Force of Vapour.	Temp.	Force of Vapour.
34°	6.20	32°	0.40	193.3°	46.60	316	30.00
44	8.10	40	0.56	196.3	50.10	320	31.70
54	10.30	45	0.70	200	53.00	325	34.00
64	13.00	50	0.86	206	60.10	330	36.40
74	16.10	55	1.00	210	65.00	335	38.90
84	20.00	60	1.23	214	69.30	340	41.60
94	24.70	65	1.49	216	72.20	345	44.10
104	30.00	70	1.76	220	78.50	350	46.86
105	30.00	75	2.10	225	87.50	355	50.20
110	32.54	80	2.45	230	94.10	360	53.30
115	35.90	85	2.93	232	97.10	365	56.90
120	39.47	90	3.40	236	103.60	370	60.70
125	43.24	95	3.90	238	106.90	372	61.90
130	47.14	100	4.50	240	111.24	375	64.00
135	51.90	105	5.20	244	118.20	Oil of Turpentine.	
140	56.90	110	6.00	247	122.10	Temp.	Force of Vapour.
145	62.10	115	7.10	248	126.10		
150	67.60	120	8.10	249.7	131.40	304	30.00
155	73.60	125	9.25	250	132.30	307.6	32.60
160	80.30	130	10.60	252	138.60	310	33.50
165	86.40	135	12.15	254.3	143.70	315	35.20
170	92.80	140	13.90	258.6	151.60	320	37.06
175	99.10	145	15.95	260	155.20	322	37.80
180	108.30	150	18.00	262	161.40	326	40.20
185	116.10	155	20.30	264	166.10	330	42.10
190	124.80	160	22.60			336	45.00
195	133.70	165	25.40			340	47.30
200	142.80	170	28.30			343	49.40
205	151.30	173	30.00			347	51.70
210	166.00	178.3	33.50			350	53.80
		180	34.73			354	56.60
		182.3	36.40			357	58.70
		185.3	39.90			360	60.80
		190	43.20			362	62.40



TABLE IV.

*Dr Ure's Table of the quantity of Oil of Vitriol, of sp. gr. 1.8485, and of Anhydrous Acid, in 100 parts of dilute Sulphuric Acid, at different densities.*

Liquid.	Sp.Gr.	Dry.	Liquid.	Sp.Gr.	Dry.	Liquid.	Sp.Gr.	Dry.
100	1.8485	81.54	66	1.5503	53.82	32	1.2334	26.09
99	1.8475	80.72	65	1.5390	53.00	31	1.2260	25.28
98	1.8460	79.90	64	1.5280	52.18	30	1.2184	24.46
97	1.8439	79.09	63	1.5170	51.37	29	1.2108	23.65
96	1.8410	78.28	62	1.5066	50.55	28	1.2032	22.83
95	1.8376	77.46	61	1.4960	49.74	27	1.1956	22.01
94	1.8336	76.65	60	1.4860	48.92	26	1.1876	21.20
93	1.8290	75.83	59	1.4760	48.11	25	1.1792	20.38
92	1.8233	75.02	58	1.4660	47.29	24	1.1706	19.57
91	1.8179	74.20	57	1.4560	46.48	23	1.1626	18.75
90	1.8115	73.39	56	1.4460	45.66	22	1.1549	17.94
89	1.8043	72.57	55	1.4360	44.85	21	1.1480	17.12
88	1.7962	71.75	54	1.4265	44.03	20	1.1410	16.31
87	1.7870	70.94	53	1.4170	43.22	19	1.1330	15.49
86	1.7774	70.12	52	1.4073	42.40	18	1.1246	14.68
85	1.7673	69.31	51	1.3977	41.58	17	1.1165	13.86
84	1.7570	68.49	50	1.3884	40.77	16	1.1090	13.05
83	1.7465	67.68	49	1.3788	39.95	15	1.1019	12.23
82	1.7360	66.86	48	1.3697	39.14	14	1.0953	11.41
81	1.7245	66.05	47	1.3612	38.32	13	1.0887	10.60
80	1.7120	65.23	46	1.3530	37.51	12	1.0809	9.78
79	1.6993	64.42	45	1.3440	36.69	11	1.0743	8.97
78	1.6870	63.60	44	1.3345	35.88	10	1.0682	8.15
77	1.6750	62.78	43	1.3255	35.06	9	1.0614	7.34
76	1.6630	61.97	42	1.3165	34.25	8	1.0544	6.52
75	1.6520	61.15	41	1.3080	33.43	7	1.0477	5.71
74	1.6415	60.34	40	1.2999	32.61	6	1.0405	4.89
73	1.6321	59.52	39	1.2913	31.80	5	1.0336	4.08
72	1.6204	58.71	38	1.2826	30.98	4	1.0268	3.26
71	1.6090	57.89	37	1.2740	30.17	3	1.0206	2.446
70	1.5975	57.08	36	1.2654	29.35	2	1.0140	1.63
69	1.5868	56.26	35	1.2572	28.54	1	1.0074	0.8154
68	1.5760	55.45	34	1.2490	27.72			
67	1.5648	54.63	33	1.2409	26.91			

TABLE V.

*Dr Ure's Table of the quantity of Real or Anhydrous Nitric Acid in 100 parts of Liquid Acid, at different densities.*

Specific Gravity.	Real acid in 100 parts of the Liq.	Specific Gravity.	Real acid in 100 parts of the Liq.	Specific Gravity.	Real acid in 100 parts of the Liq.	Specific Gravity.	Real acid in 100 parts of the Liq.
1.5000	79.700	1.4189	59.775	1.2947	39.850	1.1403	19.925
1.4980	78.903	1.4147	58.978	1.2887	39.053	1.1345	19.128
1.4960	78.106	1.4107	58.181	1.2826	38.256	1.1286	18.331
1.4940	77.309	1.4065	57.384	1.2765	37.459	1.1227	17.534
1.4910	76.512	1.4023	56.587	1.2705	36.662	1.1168	16.737
1.4880	75.715	1.3973	55.790	1.2644	35.865	1.1109	15.940
1.4850	74.918	1.3948	54.993	1.2583	35.068	1.1051	15.143
1.4820	74.121	1.3882	54.196	1.2528	34.271	1.0993	14.346
1.4790	73.324	1.3833	53.399	1.2462	33.474	1.0935	13.549
1.4760	72.527	1.3783	52.602	1.2402	32.677	1.0878	12.752
1.4730	71.730	1.3732	51.805	1.2341	31.880	1.0821	11.955
1.4700	70.933	1.3681	51.068	1.2277	31.083	1.0764	11.158
1.4670	70.136	1.3630	50.211	1.2212	30.286	1.0708	10.361
1.4640	69.339	1.3579	49.414	1.2148	29.489	1.0651	9.564
1.4600	68.542	1.3529	48.617	1.2084	28.692	1.0595	8.767
1.4570	67.745	1.3477	47.820	1.2019	27.895	1.0540	7.970
1.4530	66.948	1.3427	47.023	1.1958	27.098	1.0485	7.273
1.4500	66.155	1.3376	46.226	1.1895	26.301	1.0430	6.376
1.4460	65.354	1.3323	45.429	1.1833	25.504	1.0375	5.579
1.4424	64.557	1.3270	44.632	1.1770	24.707	1.0320	4.782
1.4385	63.760	1.3216	43.835	1.1709	23.910	1.0267	3.985
1.4346	62.963	1.3163	43.038	1.1648	23.113	1.0212	3.188
1.4306	62.166	1.3110	42.241	1.1587	22.316	1.0159	2.391
1.4269	61.369	1.3056	41.444	1.1526	21.519	1.0106	1.594
1.4228	60.572	1.3001	40.647	1.1465	20.722	1.0053	0.797

TABLE VI.

*Tables showing the Specific Gravity of Liquids, at the Temperature of 55° Fahr. corresponding to the degrees of Baumé's Hydrometer.*

FOR LIQUIDS LIGHTER THAN WATER.

Deg.	Sp. Gr.	Deg.	Sp. Gr.	Deg.	Sp. Gr.	Deg.	Sp. Gr.	Deg.	Sp. Gr.
10	= 1.000	17	= .949	23	= .909	29	= .874	35	= .842
11	.990	18	.942	24	.903	30	.867	36	.837
12	.985	19	.935	25	.897	31	.861	37	.832
13	.977	20	.928	26	.892	32	.856	38	.827
14	.970	21	.922	27	.886	33	.852	39	.822
15	.963	22	.915	28	.880	34	.847	40	.817
16	.955								

TABLE VI. CONTINUED.

## FOR LIQUIDS HEAVIER THAN WATER.

Deg. Sp. Gr.	Deg. Sp. Gr.	Deg. Sp. Gr.	Deg. Sp. Gr.	Deg. Sp. Gr.
0=1.000	15=1.114	30=1.261	45=1.455	60=1.717
3 1.020	18 1.140	33 1.295	48 1.500	63 1.779
6 1.040	21 1.170	36 1.333	51 1.547	66 1.848
9 1.064	24 1.200	39 1.373	54 1.594	69 1.920
12 1.089	27 1.230	42 1.414	57 1.659	72 2.000



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